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Research article

Ecological and human health risk assessment of total petroleum hydrocarbons in surface water and sediment from Woji Creek in the Niger Delta Estuary of Rivers State, Nigeria

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ABSTRACT

This study was designed to assess total petroleum hydrocarbon (THP) concentrations in the surface water and sediment sampled from Woji Creek and to assess potential ecological and human health risk due to petroleum hydrocarbons along the creek. Physicochemical parameters [pH, temperature (T), electrical conductivity (EC), dissolved oxygen (DO), total dissolved solids (TDS)] were in-situ measured from sediment and surface water; hydrological parameters (width, depth and volume) were used to calculate the flow rate (discharge) at different stations of the creek. Trend of TPH in the surface water samples along the creek were as follows: St4 (3.639 ± 1.121 mg/L) > St3 (2.449 ± 0.623 mg/L) > St1 (1.457 ± 0.244 mg/L) > St2 (1.069 ± 0.228 mg/L) > St5 (1.010 ± 0.120 mg/L) Trend of TPH concentration across the creek was as follows: St1 - 8.758 ± 0.697 mg/kg > St3 - 7.675 ± 0.541 mg/kg > St5 - 5.515 ± 0.401 mg/kg > St4 - 5.075 ± 0.363 mg/kg > St2 - 3.162 ± 0.307 mg/kg. Diagnostic indices indicate that the hydrocarbon in the creek was from petrogenic source. Estimation of ecological risk indicated risk in the surface water but not in the sediment. However, human health risk assessment indicated no risk due to human ingestion of the sediment or surface water.

1. Introduction

An estuary is usually defined as an enclosed body of water with a direct connection to the open sea and influenced by tidal flow (Adey and Loveland, 2007). Estuaries are the sites where freshwater flowing from the land as runoffs and salt water flowing from the sea meet (Balasuriya, 2018). Ecologically they may be referred to as the nurseries of the sea because some marine organisms reproduce and spend their early lives there (NOAA, 2020a). This is made possible by the rising tide which keeps the estuarine salinity high enough and shallow hydrology which creates an oxygen-rich environment, both of which are essential for their survivals (Adey and Loveland, 2007). The Niger Delta Estuary makes up about 60 % of the estuaries in Nigeria; the largest of these estuaries is the Bonny Estuary (Zabbey et al., 2019). The physicochemical and hydrological characteristics of estuaries provide essential habitat for birds, fish, amphibians, insects, invertebrates and other wildlife; this makes estuarine ecosystems economically important (NOAA, 2020b).

Petroleum occurs naturally composing predominantly of carbon and hydrogen and little amounts of other elements such as sulphur, nitrogen and oxygen (Dembicki Harry, 2017). Hydrocarbons are the most abundant compounds in petroleum; they are either saturated (hydrogen-containing carbon-to-carbon single bonds) or unsaturated (hydrogen-containing at least one carbon-to-carbon double or triple bond) (Speight, 2017). Hydrocarbons are released naturally into the

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environment from the decomposition of organic matter, they are also released through anthropogenic activities such as petroleum exploration and the burning of fossil fuels (Brusseau et al., 2019).

Total petroleum hydrocarbons (TPH) is a term used to describe petroleum-based hydrocarbons found in crude that can be measured in environmental media; They are a combination of different fractions of petroleum hydrocarbons (ASTDR, 1999). Petroleum hydrocarbons (PHs) are petroleum compounds made entirely of carbon and hydrogen; they consist of hydrocarbons with a broad range of molecular weights. PHs are divided into alkanes (or paraffins), cycloalkanes (or naphthalenes), alkenes (or olefins) and arenes (or aromatics) (Kuppusamy et al., 2020a). Although some hydrocarbon fractions can be degraded by microorganisms, large chain aliphatic and aromatic hydrocarbons can persist in the environment and cause environmental problems (Hasanuzzaman et al., 2007). Refined petroleum hydrocarbons are highly lipophilic and volatile, this promotes their ability to be absorbed through the lungs and gastrointestinal tract or organisms (Dalefield, 2017). When PHs enter into aquatic ecosystems, they can cause great harm to organisms; they pose acute to chronic toxicity to organisms depending on their metabolism and photooxidation (Kuppusamy et al., 2020b). PHs can bioaccumulate in larger organisms through trophic transfer by the ingestion of lower organisms or through direct ingestion by the adsorption of HCs on organic matter (Quintana-Rizzo et al., 2015). Sediment chronic toxicity assessment carried out by Scarlett et al. (2007) revealed that oil spills can reduce the growth of amphipods. Another study discovered that halogenated aliphatic hydrocarbons showed the ability to initiate lipid peroxidation and to disturb chromosome segregation at mitosis (Crebelli et al., 1995).

In addition to causing a nuisance in surface water, hydrocarbons can be bioaccumulated in aquatic biota. A report of water quality in samples collected from Ayetoro within the coastal area of Ondo State (Ilaje Local Government Area) between November 2017 and April 2018 has mean total petroleum hydrocarbon values of 4.07 ± 1.21 mg/l (Akinola et al., 2019). Sediment samples of Algoa Bay in the Eastern Cape Province of South Africa recorded total petroleum hydrocarbon (TPH) values varying from 45.07 to 307 μg/l in the water and 0.72–27.03 mg/kg in the sediments (Adeniji et al., 2017a, b). Levels of total hydrocarbon in water and sediment of a polluted tidal creek, Bonny River, Niger Delta, Nigeria were analysed, the concentration of total hydrocarbon content in water and sediment varied from 15.6 ± 1.86–23.4 ± 2.55 mg/l and 1,403 ± 80.61–3,755 ± 113.14 mg/kg respectively; this was above the established permissible levels of 10 mg/l in water and 30 mg/kg in sediment (Wokoma, 2014). In soft sediment, TPH has been recorded to have a negative correlation with species abundance and richness of sediment macroinvertebrates (Lu, 2005).

The Niger Delta region of Nigeria is the major hydrocarbon deposit in Nigeria; the region has had several hydrocarbon drilling and production sites both on- and off-shore. In recent years, attention has been brought to the devastation brought about by accidental spills in the region which has led to wide-ranging ecological pollution (UNEP, 2011). However, although petroleum exploration in Nigeria is governed by legislation that is designed to manage environmental issues, illegal petroleum activities are not governed by these laws. Bunkering activities, which encompasses diversion and smuggling of oil and unauthorized loading of ships, is a major source through which the country loses oil and a major source of oil spill leading to environmental damage in the Niger Delta (Anyio, 2015; Vreÿ, 2012). Studies carried out by Ihunwo et al. (2019) detected high concentrations of polycyclic aromatic hydrocarbons in sediment and surface water from Woji Creek due to accidental spill related to bunkering activities. Further studies also recorded that the concentration of PAH determined in the surface water and sediment will have a detrimental effect on human health and ecology (Ihunwo et al., 2021). Therefore, this study aims to determine the concentrations of petroleum hydrocarbons (PHs) (aliphatic hydrocarbons) in surface water and sediment in the creek and assess potential source of PH and, ecological and human health risk due to PHs in sediments and surface water.

2. Material and methods

2.1. Study area

Woji Creek is an estuary in Rivers State, Nigeria, which runs intertidally carrying more saline water from downstream (the North Atlantic Ocean) and freshwater from upstream (Figure 1). The creek serves as a route of transportation into the city by water transport through the Bright of Bonny into the City of Port Harcourt. For this reason, boats and barges are manufactured and maintained at several points along the creek, therefore creating a potential for pollution due to these anthropogenic activities (Dibofori- Orji et al., 2019; Ibezim-Ezeani and Ihunwo, 2020). Fishing is also a major use of the creek by local communities. The river flows from St1 upstream to St5 downstream. There are 2 major sites of boat and barge manufacture, at St3 and between St4 and St5. St3 is close to an abattoir and the Port Harcourt Zoo; periodically, scrap metals and plastics are loaded off and on boats for further transportation in and out of Rivers State. Being one of the routes by water into the city of Port Harcourt, periodic hydrocarbon spills have been observed and attributed to bunkering activities.

2.2. Sample collection

With the aid of a boat and Van Veen grab sampler, weekly samples of surface water and sediment were collected from five stations identified along the creek. Sediment was sampled from the intertidal zone of the creek at a depth of ≈ 5cm. Surface water was sampled using a peristaltic pump with a Teflon tube from the surface and a depth of ≈50 cm; both samples were mixed to form a composite sample for each station. Sampling was done for four months (June–September 2019), these months cover the rainy season of the study area (NiMet, 2020). Five samples were collected transversely at each station and mixed thoroughly to make a composite sample of each station (Patil, 2002). Water was put into a 1000 ml well-labelled bottle and sediment samples were put into well-labelled Ziploc bags; samples were then placed inside coolers with ice in the bottom and on the top. Samples were transported immediately to the laboratory for analysis.

Physicochemical parameters [(pH, temperature (T), electrical conductivity (EC), dissolved oxygen (DO), total dissolved solids (TDS)] – surface water [(pH, temperature (T), electrical conductivity (EC)] – sediment) were in-situ measured using a multiparameter sonde (Ip67 Combo pH/Conductivity/Salinity/DO Meter Model 8603) and a TDS tester (HM Digital TDS-EZ).

The hydrological parameters (width, depth and velocity) were used to calculate the flow rate (discharge) at different stations of the creek using the Velocity-Area method (Turnipseed and Sauer, 2010) shown in Eq. (1):

$$Q = \sum_{i=1}^{n} a_i v_i \qquad \text{eq.1}$$

Where Q is the total discharge or total flowrate (m^3/s).

a_i is the cross-sectional area for the *i*th segment of the creek (m^2)
v_i is the mean velocity of the water at the *i*th segment of the creek (m/s)

2.3. Sample extraction and analysis

Apparatus used in the laboratory were as follows: weighing balance, pestle and mortar, spatula-stainless steel, test sieves, micro-syringes, vials, glassware, 1 L volumetric flask, pipettes and burette, conical and volumetric flask. Reagents used were anhydrous sodium sulphate, dichloromethane and hexane (Ratio 1:1), activated silica gel (Ihunwo et al., 2021).

10 g of sediment sample was weighed into a 50 mL extraction bottle, 30 mL of dichloromethane (extraction solvent) was poured into the bottle

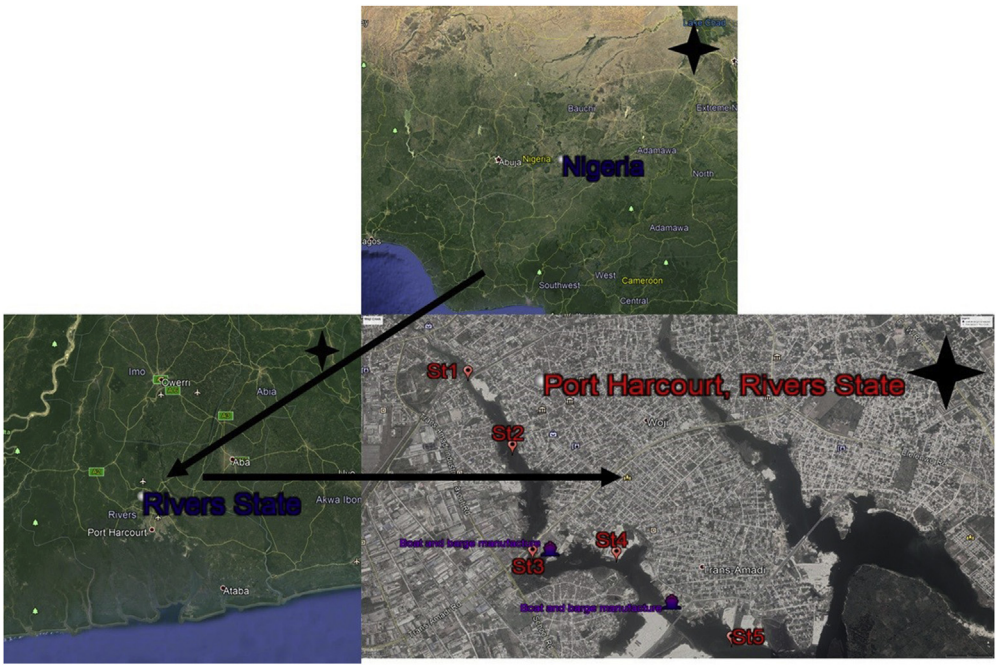

Figure 1. Sample stations along Woji Creek in Woji Town, Port Harcourt City, Rivers State Nigeria.

and vigorously shaken for 2 min and allowed to extract. After the solid phase settles, the extracted mixture is filtered through a filter paper containing, 5 g of activated silica gel and 5 g of sodium sulphate into the vial. A known volume of water sample and dichloromethane was poured into a separatory funnel and vigorously shaken for 2 min. The organic later was allowed to separate from the water and filtered through a filter paper containing, 5 g of activated silica gel and 5 g of sodium sulphate into the vial. Relatively dark extracted 5–10 mL of samples were diluted with dichloromethane (Ilavsk and Hriv, 2004; USEPA, 1999). Extracted samples were analysed using an Agilent 7890A Gas Chromatograph.

Table 1 shows the target hydrocarbons.

2.4. Quality assurance and quality control (QA/QC)

Quality control and quality assurance were carried out through the work process. The sampling equipment to be used was first washed with laboratory-grade detergent and clean water, then rinsed thrice with Milli-Q. Further rinsing was done using methanol, then Capillary GC pesticide residue grade methylene chloride and allowed to dry before use. All in-situ equipment used was calibrated. Verification of system calibration was done, making sure that the calibration range consists of no less than three linear concentration points. Blank or zero analyte samples were run, and assessment of bias was performed by analysing in duplicate. GC detection limits for hydrocarbon analyses were 0.00001 ppm (Ihunwo et al., 2021).

Standard used for QA/QC laboratory analysis was the C8–C40, Cat. No. DRH-008S-R2 certified reference material produced by AccuStandard in New Heaven Connecticut, United States of America. The standard had a concentration of 500 μg/mL in Chloroform. Each component of hydrocarbon had a target concentration of 500 μg/mL % recovery of each component was as follows: n-Octane – 99.3 %, n-Nonane – 98.5 %, n-Decane – 100 %, n-Undecane – 99.9 %, n-Dodecane – 99.2 %, n-Tridecane – 99.1 % n-Tetradecane – 100 %, n-Pentadecane – 100.4 %, n-Hexadecane – 98 %, n-Heptadecane – 99.9 %, Pristane - 92.6 %, n-Octadecane – 100 %, Phytane - 102 %, n-Nonadecane – 94.9 %, n-Eicosane – 99.4 %, n-Heneicosane – 99.9 %, n-Docosane – 99.0 %, n-Tricosane – 100 %, n-Tetracosane – 100 %, n-Pentacosane – 105 %, n-Hexacosane – 93 %, n-Heptacosane – 97.5 %, n-Octacosane – 99.4 %, n-Nonacosane – 99.1 %, n-Triacontane – 99.9 %, n-Hentriacontane – 99.5 %, n-Dotriacontane - 99.6 %, n-Tritriacontane – 97.9 %, n-Tetratriacontane – 99.0 %, n-Pentatriacontane – 100 %, n-Hexatriacontane – 100.1 %, n Heptatriacontane – 99.9 %, n-Octatriacontane – 99.8 %, n-Nonatriacontane – 100.1 %, n-Tetracontane – 100 %.

2.5. Data analysis

Analysis of variance was performed to assess the statistically significant difference in PH concentrations in the surface water and sediment between stations using Past Statistics version 4.02. Pearson's correlation analysis was also performed to assess the correlation between the river in situ parameters, hydrological parameters and TPH in the surface water and sediment; data was initially log-transformed before analysis using Past Statistics (Hammer, 2020).

2.5.1. Ecological risk assessment

According to Arzaghi et al. (2018), ecological risk assessment (ERA) was determined using Eq. (2):

$$HQ = \frac{\text{Measured environmental concentration of individual hydrocarbon}}{\text{Toxicity reference value}} \quad \text{eq. 2}$$

Hazard index (HI) is the sum of the hazard quotient (HQ) of individual hydrocarbons. HI (HQ) ≥ 1 is high risk; $0.1 = \text{HI (HQ)} < 1$ is medium risk; and HI (HQ) < 0.1 is low risk (Gao et al., 2014; Tian et al.,

2020). Toxicity reference value (TRV) for surface water was obtained from the Hawaii Department of Health; TRV for surface water = 0.64 mg/l for $C_{14} - C_{28}$ (HIDOH, 2017). TRV for sediment was obtained from Massachusetts department of environmental protection; TRV for sediment = 5.54 mg/kg for $C_{14} - C_{18}$ and 9.88 mg/kg for $C_{19} - C_{36}$ (MassDEP, 2007).

2.5.2. Human health risk assessment

Human health risk assessment was carried out using the "fractionation method" where aliphatic or aromatic compounds are divided into several defined carbon ranges (ITRC, 2018). Through this means, oral and inhalation toxicity values are assigned to each group based on values surrogate or components. Low carbon range (LCR): $C_5 - C_8$ are grouped as n-hexane, medium carbon range (MCR): $C_9 - C_{18}$ are grouped as hydrocarbon streams or solvents within the range and containing <1 % aromatics, and high carbon range (HCR): $C_{19} - C_{32}$ are grouped as mineral oils.

Human health risk due to oral intake of petroleum hydrocarbons from surface water and sediment was assessed for children and adults with Eq. (1):

$$Intake\ (oral) = \frac{C_i \times IR \times ED}{BW \times AT} \quad \text{eq. 3}$$

Where C_i is the concentration of the individual hydrocarbon compound in water and sediment, ED is the exposure duration (children – 9 years, adults – 6 years), EV is the event frequency (children and adults – 1 event/day), BW is the body weight (children – 15 kg, adults – 70 kg), AT is average time (day/year) (ED x 365 days) (U.S. EPA, 2004). IR is the ingestion rate for water and sediment. According to Dorevitch et al. (2011), water ingestion rates from fishing on surface water is estimated as 0.0864 L/d, while Wilson et al. (2015) estimated sediment ingestion rate due to surface water intake as 74.4 mg/d for all ages.

Risk characterisation was calculated using Eq. (4) for noncancer:

$$HI_{oral} = \sum \left[\frac{Intake\ (oral)}{RfD}\right]_i \quad \text{eq. 4}$$

Oral noncancer reference dose, RfD (mg/kg-day), used for LCR, MCR and HCR were 0.3 (U.S. EPA, 2009a), 0.1 (U.S. EPA, 2009b) and 30 (U.S. EPA, 2009c) respectively.

Table 1. Target n- Hydrocarbons molecular formula and weight analysed in samples from the Woji creek.

Hydrocarbon	Molecular formula	Molecular weight (g/mol)
Octane (C_8)	$CH_3(CH_2)_6CH_3$	114.23
Nonane (C_9)	$CH_3(CH_2)_7CH_3$	128.26
Decane (C_{10})	$CH_3(CH_2)_8CH_3$	142.28
Undecane (C_{11})	$CH_3(CH_2)_9CH_3$	156.31
Dodecane (C_{12})	$CH_3(CH_2)_{10}CH_3$	170.33
Tridecane (C_{13})	$CH_3(CH_2)_{11}CH_3$	184.36
Tetradecane (C_{14})	$CH_3(CH_2)_{12}CH_3$	198.39
Pentadecane (C_{15})	$CH_3(CH_2)_{13}CH_3$	212.41
Hexadecane (C_{16})	$CH_3(CH_2)_{14}CH_3$	226.44
Heptadecane (C_{17})	$CH_3(CH_2)_{15}CH_3$	240.47
Pristane	$(CH_3)_2CH(CH_2)_3CH(CH_3)$ $(CH_2)_3CH(CH_3)$ $(CH_2)_3CH(CH_3)_2$	268.52
Octadecane (C_{18})	$CH_3(CH_2)_{16}CH_3$	254.49
Phytane	$C_{20}H_{42}$	282.55
Nonadecane (C_{19})	$CH_3(CH_2)_{17}CH_3$	268.52
Eicosane (C_{20})	$C_{20}H_{42}$	282.55
Heneicosane (C_{21})	$CH_3(CH_2)_{19}CH_3$	296.57
Docosane (C_{22})	$CH_3(CH_2)_{20}CH_3$	310.60
Tricosane (C_{23})	$CH_3(CH_2)_{21}CH_3$	324.63
Tetracosane (C_{24})	$CH_3(CH_2)_{22}CH_3$	338.65
Pentacosane (C_{25})	$CH_3(CH_2)_{23}CH_3$	352.68
Hexacosane (C_{26})	$CH_3(CH_2)_{24}CH_3$	366.71
Heptacosane (C_{27})	$CH_3(CH_2)_{25}CH_3$	380.73
Octacosane (C_{28})	$CH_3(CH_2)_{26}CH_3$	394.76
Nonacosane (C_{29})	$CH_3(CH_2)_{27}CH_3$	408.79
Triacontane (C_{30})	$CH_3(CH_2)_{28}CH_3$	422.81
Hentriacontane (C_{31})	$CH_3(CH_2)_{29}CH_3$	436.84
Dotriacontane (C_{32})	$CH_3(CH_2)_{30}CH_3$	450.87
Tritriacontane (C_{33})	$CH_3(CH_2)_{31}CH_3$	464.89
Tetratriacontane (C_{34})	$CH_3(CH_2)_{32}CH_3$	478.92
Pentatriacontane (C_{35})	$CH_3(CH_2)_{33}CH_3$	492.95
Hexatriacontane (C_{36})	$CH_3(CH_2)_{34}CH_3$	506.97
Heptatriacontane (C_{37})	$CH_3(CH_2)_{35}CH_3$	521.02
Octatriacontane (C_{38})	$CH_3(CH_2)_{36}CH_3$	535.03
Nonatriacontane (C_{39})	$CH_3(CH_2)_{37}CH_3$	549.05
Tetracontane (C_{40})	$CH_3(CH_2)_{38}CH_3$	563.08

3. Results

3.1. Physicochemical parameters in surface water and sediment, and hydrological values

Range (mean) of physicochemical properties of surface water were as follows EC: 780–5400 (2799.95 ± 366.38) μS/cm, Temp: 22.0–29.0 (25.50 ± 0.44) ºC, DO: 4.7–15.0 (8.32 ± 0.62) mg/L, pH: 5.5–9.3 (6.82 ± 0.17), ORP: 110–160 (138.00 ± 3.81) mV, TDS: 320–5300 (1650.33 ± 326.24) mg/L (Figure 2 a – f). In the sediment (Figure 2 g – i), range (mean) of physicochemical properties were as follows: pH: 6.7–7.9 (7.15 ± 0.11), EC: 920–9200 (4650.50 ± 673.88) μS/cm, ORP: 22–77 (43.75 ± 4.41) mV. Mean river hydrology values of Woji Creek were 2.67 ± 0.13 m, 79.40 ± 4.66 m, 2365.31 ± 228.19 m^3, 59.08 ± 6.03 m^3/s for depth, width, volume and flow rate respectively (Figure 3 a – d).

3.2. Petroleum hydrocarbon distribution in surface water and sediment

In surface water, the numbers of hydrocarbons identified were: St1 – 16, St2 – 16, St3 – 21, St4 – 23, St5 – 16. At St1, hydrocarbons C21 – C28 had the highest concentrations of hydrocarbons identified; C8 – C15, Pr, Ph, C32 – C38 were below the detectable limit. At St2, the highest concentrations of hydrocarbons were measured for C24 – C28; similar to St1, C8 – C15, Pr, Ph, C32 – C38 were also below the detectable limit. Hydrocarbons C18 – C24 had the highest concentrations at St3; Pr and Ph were identified at this station, however, C8 – C13, C32 and C34 – C38 were all below the detectable limit. St St4, hydrocarbons C14 – C34 were identified in the surface water; the lowest concentrations of hydrocarbons were C14, Ph, C30 – C34. At St5, C8 – C15, Pr, Ph, C32 – C38 were below the detectable limit; however, hydrocarbons C22 – C29 were the hydrocarbons with the highest concentrations at this station (Table 2).

Σ C15 – C20 was higher than Σ C23 – C33 at St3 (0.94 and 0.88 respectively) and St4 (1.80 and 1.30 respectively); however, the reverse was observed at St1 (0.37 and 0.87 respectively), St2 (0.26 and 0.66 respectively) and St5 (0.23 and 0.64 respectively). % C15 – C20 and % C23 – C33 were as follows: St1 – 25.5 % and 60.0 % respectively, St2 – 24.4 % and 61.7 % respectively, St3 – 38.4 % and 36.3 % respectively, St4 – 48.2 % and 35.8 % respectively, and St5 – 23.1 % and 63.7 % respectively. Ratio of low molecular weight (LMW) to high molecular weight (HMW) hydrocarbons (LMW/HMW) across the creek was estimated as 2.43, 2.17, 5.73, 5.31 and 2.11 for St1, St2, St3, St4 and St5 respectively. Carbon preference indices (CPI) across the creek were as follows: St1 – 0.95, St2 – 0.96, St3 – 1.04, St4 – 1.06, St5 – 0.96. Terrigenous/aquatic n-alkane ratio (TAR) values estimated across the creek were as follows: St1 - 1.18, St2 – 1.30, St3 – 0.35, St4 – 0.30, St5 –

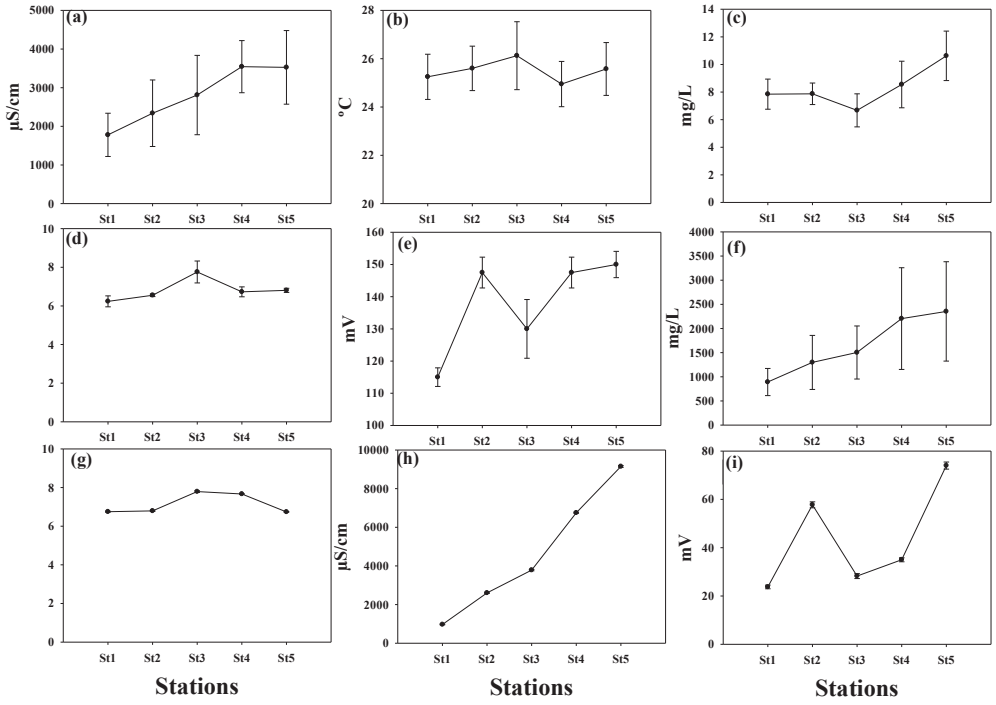

Figure 2. Physicochemical in-situ parameters of surface water (a – EC (µS/cm), b – Temp (°C), c – DO (mg/L), d – pH, e – ORP (mV), f – TDS (mg/L)) and sediment (g – pH, h – EC (µS/cm), i – ORP (mV)) of Woji Creek.

1.39. The ratio of C29/C17 across the creek were as follows: St1 - 1.98, St2 - 2.08, St3 - 1.30, St4 - 0.55 and St5 - 2.21 (Table 2).

A total of 25 hydrocarbons were detected at St1; the highest concentrations of hydrocarbons were C19–0.410 ± 0.051 mg/kg, C20–0.418 ± 0.034 mg/kg, C21–0.449 ± 0.031 mg/kg, C22–0.502 ± 0.048 mg/kg, C23–0.542 ± 0.041 mg/kg, C24–0.462 ± 0.022 mg/kg, C25–0.527 ± 0.017 mg/kg, C26–0.505 ± 0.018 mg/k, C27–0.726 ± 0.022 mg/kg, C28–0.584 ± 0.031 mg/kg, C29–0.634 ± 0.048 mg/kg, C30–0.521 ± 0.045 mg/kg. At St2, 21 hydrocarbons were detected; the highest concentration of hydrocarbon was C25 (0.254 ± 0.011 mg/kg) and the lowest concentration was C34 (0.019 ± 0.001 mg/kg). At St3, C8 – C13, C37 and C38 were not identified in the sediment samples analysed; C27 (0.644 ± 0.032 mg/kg) had the highest concentration while C36 (0.007 ± 0.001 mg/kg) has the least concentration at this station. C8 – C14, C37 and C38 were not detected at St4 sediment samples; C32, C33, C34, C35 and C36 had the least concentrations of hydrocarbons - 0.085 ± 0.014

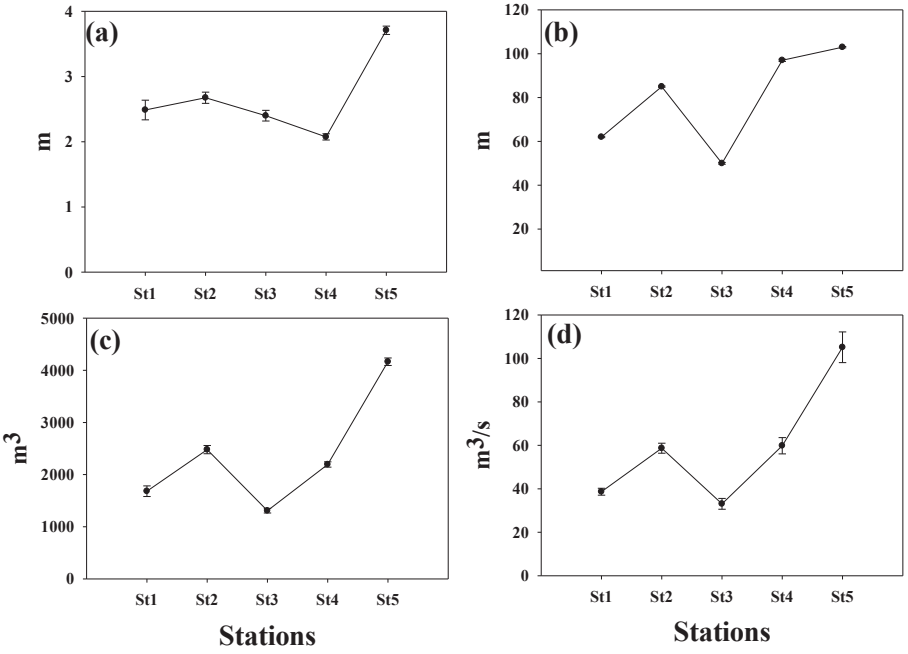

Figure 3. River hydrology (a – Depth (m), b – Width (m), c – Volume (m^3) d – Flow rate (m^3/s)) of Woji Creek.

mg/kg, 0.047 ± 0.015 mg/kg, 0.024 ± 0.011 mg/kg, 0.015 ± 0.004 mg/kg and 0.006 ± 0.001 mg/kg respectively. Similar to St1 and St3, 25 hydrocarbons were detected in sediment samples collected at St5, and C8 – C13, C37 and C38 were below detectable limit (Table 3).

Values of Σ C15 – C20 estimated across the creek were 2.07, 0.79, 1.79, 1.34 and 1.24 at St1, St2, St3, St4 and St5 respectively; values of Σ C23 – C33 estimated across the creek were 5.15, 1.99, 4.54, 3.11 and 3.51 at St1, St2, St3, St4 and St5 respectively. Estimated % C15 – C20 (% C23 – C33) at St1, St2, St3, St4 and St5 were 23.7 % (58.8 %), 24.9 % (62.8 %), 23.3 % (59.1 %), 26.4 % (61.2 %) and 22.5 % (63.7 %) respectively. Values of LMW/HMW ratio estimated across the creek were 1.38, 1.77, 1.42, 1.77 and 1.05 at St1, St2, St3, St4 and St5 respectively, while values of CPI across the creek were 1.14, 1.01, 1.13, 1.12 and 1.03 at St1, St2, St3, St4 and St5 respectively. TAR across the creek were 1.11 (St1), 1.04 (St2), 1.13 (St3), 1.04 (St4), -0.06 (St5). Ratios of C29/C17 (C17/Pr) at St1, St2, St3, St4 and St4 were 2.69 (2.34), 2.41 (1.99), 2.56 (3.28), 2.40 (3.42) and 2.14 (0.94) respectively. C18/Ph were not estimated for St2; however, values of the ratio were 6.18 at St1, 7.87 at St3, 0.15 at St4 and 1.83 at St5 (Table 3).

Trend of TPH in the surface water samples long the creek were as follows: St4 (3.639 ± 1.121 mg/L) > St3 (2.449 ± 0.623 mg/L) > St1 (1.457 ± 0.244 mg/L) > St2 (1.069 ± 0.228 mg/L) > St5 (1.010 ± 0.120 mg/L) (Figure 4a). ANOVA results revealed statistically significant difference in TPH concentrations between stations ($p < 0.001$) in surface

Table 2. Mean concentrations of hydrocarbons (mg/l) and hydrocarbon indexes in surface water across the creek (n = 16).

Compound	St1	St2	St3	St4	St5
C_8	<DL	<DL	<DL	<DL	<DL
C_9	<DL	<DL	<DL	<DL	<DL
C_{10}	<DL	<DL	<DL	<DL	<DL
C_{11}	<DL	<DL	<DL	<DL	<DL
C_{12}	<DL	<DL	<DL	<DL	<DL
C_{13}	<DL	<DL	<DL	<DL	<DL
C_{14}	<DL	<DL	4.9E-02 ± 1.1E-02	6.6E-02 ± 9.0E-03	<DL
C_{15}	<DL	<DL	6.8E-02 ± 1.2E-02	1.4E-01 ± 3.1E-02	<DL
C_{16}	5.9E-02 ± 2.0E-03	3.8E-02 ± 9.0E-03	6.8E-02 ± 2.1E-02	2.2E-01 ± 2.9E-02	4.0E-02 ± 9.1E-03
C_{17}	5.9E-02 ± 6.0E-03	4.4E-02 ± 9.0E-03	6.9E-02 ± 9.0E-03	2.7E-01 ± 5.8E-02	3.9E-02 ± 9.5E-03
Pr	<DL	<DL	4.4E-02 ± 1.1E-02	1.9E-01 ± 4.4E-02	<DL
C_{18}	7.1E-02 ± 9.0E-03	5.0E-02 ± 1.1E-02	1.2E-01 ± 9.1E-02	2.9E-01 ± 3.3E-02	4.4E-02 ± 1.6E-02
Ph	<DL	<DL	3.9E-02 ± 9.0E-03	6.1E-02 ± 1.0E-03	<DL
C_{19}	8.7E-02 ± 3.0E-03	5.9E-02 ± 1.0E-02	2.4E-01 ± 9.2E-02	3.0E-01 ± 6.7E-02	5.3E-02 ± 1.9E-02
C_{20}	9.7E-02 ± 9.0E-03	7.0E-02 ± 1.0E-02	3.0E-01 ± 4.4E-02	2.9E-01 ± 9.0E-03	5.8E-02 ± 1.6E-03
C_{21}	1.0E-01 ± 9.0E-03	7.0E-02 ± 3.0E-02	3.0E-01 ± 9.9E-02	2.7E-01 ± 7.7E-02	6.2E-02 ± 6.1E-03
C_{22}	1.1E-01 ± 6.1E-03	7.9E-02 ± 2.0E-02	2.8E-01 ± 1.2E-02	2.5E-01 ± 9.9E-02	7.2E-02 ± 3.3E-03
C_{23}	1.0E-01 ± 1.1E-02	7.7E-02 ± 2.0E-02	2.3E-01 ± 9.4E-02	2.2E-01 ± 9.0E-03	7.5E-02 ± 1.8E-03
C_{24}	1.1E-01 ± 9.0E-03	8.0E-02 ± 9.0E-03	1.4E-01 ± 6.7E-02	2.0E-01 ± 4.1E-02	7.8E-02 ± 8.1E-03
C_{25}	1.1E-01 ± 1.6E-02	8.0E-02 ± 2.0E-02	8.8E-02 ± 3.1E-03	1.8E-01 ± 2.4E-02	8.2E-02 ± 4.4E-03
C_{26}	1.2E-01 ± 1.3E-02	8.6E-02 ± 2.0E-02	8.4E-02 ± 2.8E-03	1.6E-01 ± 1.6E-02	8.3E-02 ± 3.9E-03
C_{27}	1.2E-01 ± 3.0E-03	9.1E-02 ± 1.0E-02	8.9E-02 ± 1.8E-02	1.5E-01 ± 9.0E-03	8.5E-02 ± 6.6E-03
C_{28}	1.0E-01 ± 3.3E-02	7.9E-02 ± 9.1E-03	8.6E-02 ± 8.1E-03	1.2E-01 ± 5.1E-02	8.0E-02 ± 9.1E-03
C_{29}	9.4E-02 ± 4.0E-03	7.3E-02 ± 1.1E-02	7.5E-02 ± 7.7E-03	1.1E-01 ± 3.3E-02	7.0E-02 ± 8.1E-03
C_{30}	7.4E-02 ± 6.0E-03	6.4E-02 ± 2.1E-02	6.4E-02 ± 8.3E-03	8.2E-02 ± 3.3E-03	6.1E-02 ± 6.9E-03
C_{31}	3.8E-02 ± 9.0E-03	3.0E-02 ± 9.1E-03	3.2E-02 ± 1.8E-03	4.6E-02 ± 4.7E-03	2.8E-02 ± 6.6E-03
C_{32}	<DL	<DL	<DL	2.5E-02 ± 1.2E-02	<DL
C_{33}	<DL	<DL	4.9E-02 ± 1.1E-02	6.6E-02 ± 9.0E-03	<DL
C_{34}	<DL	<DL	<DL	1.6E-02 ± 2.6E-03	<DL
C_{35}	<DL	<DL	<DL	<DL	<DL
C_{36}	<DL	<DL	<DL	<DL	<DL
C_{37}	<DL	<DL	<DL	<DL	<DL
C_{38}	<DL	<DL	<DL	<DL	<DL
TPH	1.457 ± 0.244	1.069 ± 0.228	2.449 ± 0.623	3.639 ± 1.121	1.010 ± 0.120
Diagnostic indices					
Σ C15 – C20	0.37	0.26	0.94	1.76	0.23
Σ C23 – C33	0.87	0.66	0.89	1.302	0.64
% C15 – C20	25.53	24.36	38.39	48.23	23.08
% C23 – C33	60.03	61.70	36.25	35.77	63.66
LMW/HMW	2.43	2.17	5.73	5.31	2.11
CPI (12–36)	0.95	0.96	1.04	1.06	0.96
TAR	1.18	1.30	0.35	0.30	1.39
C29/C17	1.97	2.08	1.30	0.55	2.21
C17/Pr	-	-	1.55	1.45	-
C18/Ph	-	-	2.95	4.80	-
Pr/Ph	-	-	1.14	3.05	-

water and sediment. In the surface water, post hoc test (Tukey's pairwise) showed statistically significant difference between St4 and St1 ($p < 0.001$), St2 ($p < 0.001$), and St5 ($p < 0.001$); St3 showed statistically significant difference from St4 and St5 ($p < 0.05$) (Figure 4a).

Trend of TPH concentration in sediment across the creek was as follows: St1 - 8.758 ± 0.697 mg/kg > St3 - 7.675 ± 0.541 mg/kg > St5 - 5.515 ± 0.401 mg/kg > St4 - 5.075 ± 0.363 mg/kg > St2 - 3.162 ± 0.307 mg/kg (Figure 4b). In the sediment, ANOVA also revealed statistically significant difference between groups ($p < 0.001$). Tukey's pairwise test showed statistically significant difference in TPH concentrations at St1 and St2 ($p < 0.001$), St4 ($p < 0.001$) and St5 ($p < 0.001$). There was also statistically significant difference in TPH at St3 at St2 ($p < 0.001$), St4 ($p < 0.05$) and St5 ($p < 0.05$) (Figure 4b).

3.4. Ecological risk assessment (ERA)

In the surface water, the highest HQ at St1 was contributed by C_{24} (0.18) and the least was contributed by C_{16} and C_{17} (0.09); HI at St1 was estimated as 1.42. Similarly, at St2 the least HQ was contributed by C_{16} (0.06) and the highest HQ was contributed by C_{24} and C_{25} (0.12); HI was estimated as 1.01. At St3, HQ for C_{24}, C_{23}, C_{19}, C_{22}, C_{21} and C_{20} were estimated as: 0.22, 0.35, 0.37, 0.43, 0.46 and 0.47 respectively. At St4,

Table 3. Mean concentrations of hydrocarbons (mg/kg) and hydrocarbon indexes in sediment across the creek (n = 16).

Compound	St1	St2	St3	St4	St5
C_8	<DL	<DL	<DL	<DL	<DL
C_9	<DL	<DL	<DL	<DL	<DL
C_{10}	<DL	<DL	<DL	<DL	<DL
C_{11}	<DL	<DL	<DL	<DL	<DL
C_{12}	<DL	<DL	<DL	<DL	<DL
C_{13}	<DL	<DL	<DL	<DL	<DL
C_{14}	0.184 ± 0.034	<DL	0.151 ± 0.032	<DL	0.062 ± 0.013
C_{15}	0.203 ± 0.018	0.079 ± 0.002	0.189 ± 0.031	0.119 ± 0.017	0.125 ± 0.014
C_{16}	0.228 ± 0.047	0.091 ± 0.001	0.209 ± 0.011	0.209 ± 0.018	0.194 ± 0.004
C_{17}	0.27 ± 0.033	0.094 ± 0.031	0.252 ± 0.016	0.173 ± 0.013	0.145 ± 0.011
Pr	0.115 ± 0.049	0.047 ± 0.015	0.077 ± 0.018	0.051 ± 0.011	0.154 ± 0.016
C_{18}	0.369 ± 0.021	0.148 ± 0.021	0.298 ± 0.022	0.039 ± 0.013	0.147 ± 0.015
Ph	0.06 ± 0.004	<DL	0.038 ± 0.003	0.253 ± 0.016	0.08 ± 0.011
C_{19}	0.41 ± 0.051	0.169 ± 0.022	0.357 ± 0.018	0.241 ± 0.018	0.217 ± 0.016
C_{20}	0.418 ± 0.034	0.161 ± 0.024	0.368 ± 0.028	0.255 ± 0.022	0.179 ± 0.022
C_{21}	0.449 ± 0.031	0.176 ± 0.031	0.401 ± 0.015	0.274 ± 0.014	0.199 ± 0.026
C_{22}	0.502 ± 0.048	0.192 ± 0.018	0.452 ± 0.011	0.31 ± 0.016	0.223 ± 0.022
C_{23}	0.542 ± 0.041	0.20 ± 0.013	0.48 ± 0.031	0.326 ± 0.015	0.246 ± 0.019
C_{24}	0.462 ± 0.022	0.22 ± 0.016	0.435 ± 0.019	0.307 ± 0.014	0.286 ± 0.014
C_{25}	0.527 ± 0.017	0.254 ± 0.011	0.477 ± 0.015	0.333 ± 0.016	0.372 ± 0.025
C_{26}	0.505 ± 0.018	0.22 ± 0.014	0.464 ± 0.037	0.397 ± 0.013	0.283 ± 0.025
C_{27}	0.726 ± 0.022	0.226 ± 0.014	0.644 ± 0.032	0.417 ± 0.022	0.31 ± 0.011
C_{28}	0.584 ± 0.031	0.218 ± 0.011	0.520 ± 0.042	0.359 ± 0.031	0.286 ± 0.021
C_{29}	0.634 ± 0.048	0.226 ± 0.015	0.572 ± 0.022	0.351 ± 0.022	0.242 ± 0.028
C_{30}	0.521 ± 0.045	0.229 ± 0.022	0.435 ± 0.019	0.275 ± 0.004	0.741 ± 0.034
C_{31}	0.383 ± 0.013	0.097 ± 0.019	0.312 ± 0.037	0.212 ± 0.023	0.581 ± 0.033
C_{32}	0.149 ± 0.011	0.064 ± 0.002	0.132 ± 0.041	0.085 ± 0.014	0.10 ± 0.004
C_{33}	0.116 ± 0.015	0.032 ± 0.004	0.066 ± 0.003	0.047 ± 0.015	0.068 ± 0.001
C_{34}	0.137 ± 0.021	0.019 ± 0.001	0.057 ± 0.006	0.024 ± 0.011	0.062 ± 0.004
C_{35}	0.249 ± 0.012	<DL	0.283 ± 0.031	0.015 ± 0.004	0.143 ± 0.009
C_{36}	0.015 ± 0.011	<DL	0.007 ± 0.001	0.006 ± 0.001	0.071 ± 0.003
C_{37}	<DL	<DL	<DL	<DL	<DL
C_{38}	<DL	<DL	<DL	<DL	<DL
TPH	8.758 ± 0.697	3.162 ± 0.307	7.675 ± 0.541	5.075 ± 0.363	5.515 ± 0.401
Diagnostic indices					
Σ C15 – C20	2.07	0.79	1.79	1.34	1.24
Σ C23 – C33	5.15	1.99	4.54	3.11	3.51
% C15 – C20	23.7	24.9	23.3	26.4	22.5
% C23 – C33	58.8	62.8	59.1	61.2	63.7
LMW/HMW	1.38	1.77	1.42	1.77	1.05
CPI (12–36)	1.14	1.01	1.13	1.12	1.03
TAR	1.11	1.04	1.13	1.04	-0.06
C29/C17	2.69	2.41	2.56	2.4	2.14
C17/Pr	2.34	1.99	3.28	3.42	0.94
C18/Ph	6.18	-	7.87	0.15	1.83
Pr/Ph	1.93	-	2.02	0.20	1.91

the highest HQ was estimated for C_{19} (0.47) and the HI was 4.59, however, the lowest HI was recorded at St5 (0.94) (Table 4).

In the sediment, the highest contributors to the HI (St1 - 0.99) were C_{22}, C_{26}, C_{25}, C_{30}, C_{23}, C_{28}, C_{29}, C_{18} and C_{27} with the following HQ: 5.10E-02, 5.10E-02, 5.30E-02, 5.30E-02, 5.50E-02, 5.90E-02, 6.40E-02, 6.70E-02 and 7.40E-02 respectively. St3 had the second highest HI (0.87), contributed by C_{24}, C_{30}, C_{17}, C_{22}, C_{26}, C_{25}, C_{23}, C_{28}, C_{18}, C_{29}, C_{27} with the following values of HQ: 4.40E-02, 4.40E-02, 4.50E-02, 4.60E-02, 4.70E-02, 4.80E-02, 4.90E-02, 5.30E-02, 5.40E-02, 5.80E-02 and 6.50E-02 respectively (Table 4).

3.5. Human health risk assessment

Human health risk (hazard index [HI]) due to accidental ingestion of surface water by children from fishing was estimated as follows 3.0E-5, 2.1E-5, 6.6E-5, 1.9E-4 and 2.0E-5 for St1, St2, St3, St4 and St5 respectively; for adults HI was lower than those estimated for children – St1 - 6.5E-6, St2 - 4.6E-6, St3 - 1.4E-5, St4 - 4.0E-5 and St5 - 4.2E-6. HI estimated for oral ingestion of sediment were 1.9E-1 (St1), 6.4E-2 (St2), 1.6E-1 (St3), 8.2E-2 (St4) and 1.1E-1 (St5) for children and 3.0E-2 (St1), 9.3E-3 (St2), 2.6E-2 (St3), 1.7E-2 (St4) and 2.0E-2 (St5) (Figure 5).

3.6. Correlation

Pearson's correlation analysis showed positive correlation between TPH in the surface water and in the sediment ($r = 0.28$, $p > 0.05$). TPH in water showed statistically significant positive correlation with electric conductivity (EC) of water ($r = 0.55$, $p < 0.05$), water temperature ($r = 0.54$, $p < 0.05$), and TDS in water ($r = 0.53$, $p < 0.05$). TPH in water showed statistically significant negative correlation with dissolved oxygen (DO) in water ($r = -0.48$, $p < 0.05$). TPH in sediment showed a statistically significant negative correlation with DO in the surface water ($r = -0.48$, $p < 0.05$). TPH in sediment also showed a statistically significant positive correlation with surface water temperature ($r = 0.58$, $p < 0.05$).

DO showed statistically significant negative correlation with EC ($r = -0.60$, $p < 0.05$), temperature ($r = -0.80$, $p < 0.001$) and total dissolved solids ($r = -0.63$, $p < 0.001$) in surface water. though, TDS showed a statistically significant positive correlation with water EC ($r = 0.94$, $p < 0.001$) and water temperature ($r = 0.85$, $p < 0.001$). ORP of surface water showed statistically significant positive correlation with river width ($r = 0.66$, $p < 0.001$), volume ($r = 0.56$, $p < 0.05$) and flowrate ($r = 0.61$, $p < 0.001$). EC in sediment and ORP in sediment showed statistically significant positive correlation with ORP of surface water (EC-Sed.: $r = 0.68$, $p < 0.001$) (ORP-Sed.: $r = 0.68$, $p < 0.001$) (Table 5).

4. Discussion

Electric conductivity and total dissolved solid concentration show similarity in trend (Omer, 2019; Tchobanoglous et al., 2003; Youcai and Sheng, 2017). EC and TDS showed a general increasing trend from St1 (upstream) to St5 (downstream). In seawater and brackish water concentration of TDS is usually 1500–5000 mg/L and >5000 mg/L respectively (Moran, 2018; Omer, 2019). However, the range of TDS in domestic waste water effluent is 250–850 mg/l (Park and Snyder, 2020). Therefore, the results obtained show an influence of tidal flow carrying water with higher EC and TDS from St5 to St1 (Cochran, 2014). This is a similar trend as that observed in Anya – Ogologo River in the city of Port Harcourt which is also an estuary of Sambreiro River (Ihunwo et al., 2018; Isaiah et al., 2019). TDS in the studied creek was much higher than those measured from Nun River at Gbarantoru and Tombia Axis in Bayelsa State, Nigeria which ranged from 29.83-35.83 mg/l (Izah et al., 2018). The measure of the ability of electricity to pass through water is knowns as electric conductivity; this is affected by the input of inorganic ions carrying positive and negative charges into the water (Rich and Maier, 2015). DO in the surface water is affected by the chemical, physical, and biochemical conditions of the water (Trick et al., 2018); organic effluent input into surface water can reduce the amount of oxygen dissolved in the water by increasing the aerobic activities of microorganism in the water (Gerba and Pepper, 2015; Kalev and Toor, 2018); this could account for the lower DO observed at St3, with point source abattoir effluent, compared to other stations along the creek. According to Doble and Kumar (2005), the ease with which the molecules of water or sediment will accept electrons is knowns as the redox potential (ORP). Although ORP of surface marine sediments provides a qualitative indication of the conditions, it can play a role as an indicator or chemical changes in the sediment (Uriarte et al., 2004). As the quantity of oxygen reduces transversely in the river from surface water to sediment, the conditions of the river changes from oxidised to reduced consequently leading to a reduction in ORP values. In sediment which has a reduced condition, ORP range from >100 mv to negative value, but in surface waters with more oxygen (oxidized conditions) ORP is ~200 mV (Søndergaard, 2009). Although the ORP measured in this creek is below 200 mV, the trend stated above is similar to that of this creek; ORP measured in sediment were all below 100 mV. The lower ORP (<200 mV) could indicate a condition which hinders dissolution of oxygen (oil spill) or a condition which consumes a lot of oxygen such as microbial activities (Harrel, 1985; Uriarte et al., 2004). Along the creek, there is a continuous input of organic waste from the abattoir at St3, this, in addition to the petroleum in the creek could account for the lower ORP.

Generally, the depth of estuaries are <100 m promoting conditions of top to bottom interaction, this concept is known as benthic-pelagic coupling (Cochran, 2014). In shallow estuarine ecosystems, the accumulation of organic matter in sediment surface is high creating an increased microbial degradation activity and nutrient cycling (Hood et al., 2008). In the present study, river depth increased from St1 to St5 with the highest depth of 3.8 m. This shallow condition favours benthic-pelagic coupling and resuspension in sediment; therefore, a high rate of contaminant resuspension from sediment occurs (Beiras, 2018; Kim et al., 2020; Latimer et al., 1999). This could then a situation of continuous release of contaminant from the sediment which acts as a sink for contaminants, thereby leading to possible mobilization of contaminants (such as hydrocarbons) from the sediment into the water column (Dong et al., 2016; Guigue et al., 2017).

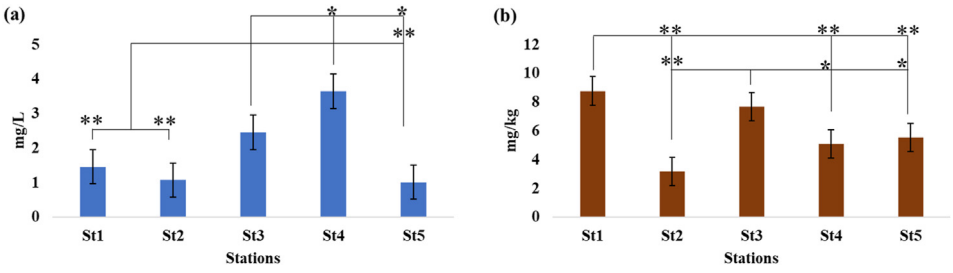

Figure 4. Concentration of total petroleum hydrocarbons in (a) surface water (mg/L) and (b) sediment (mg/kg). Statistically significant difference between stations as a result of ANOVA are represented in asterixis, $p < 0.05$ = *, $p < 0.001$ = **.

As the river flow rate increases, the quantity of materials eroded from the river bedrock increase, therefore creating a larger river width and volume (Allen et al., 2018; Lewin et al., 2018; Frasson et al., 2019). In Woji Creek, this distinctive form is observed as river depth, width, volume and flow rate increases downstream. This relation between river hydrology parameters was also observed by Pavelsky et al. (2014) in Yukon River Basin located between the Yukon Territory in Canada and Alaska. The volume of water measured in the studied creek was higher than the annual volume of water recorded at Rivers Orlie (352.33 m^3) and Edion (88225.32 m^3) in Edo State, Niger Delta, Nigeria (Emeribe et al., 2016).

According to Timis et al. (2015), the flow rate in a river increased as the flow distance increased from upstream to downstream, also the concentration of pollutants reduce as water flow from the source of input downstream. In the present study, mean flow rate measured increased in the downstream direction (from St1 – St5). The highest mean flow rate measured along the study area was 125.75 m^3/s, this was lower than the mean flow rate of the rivers in the Cantabrian shelf in Northern Greenland with a mean flow rate of 400 m^3/s because of the influence of runoff from mountain ranges (Borja et al., 2019). From 1986 – 2009, mean flow rate of Gumara River in the Blue Nile Basin in Ethiopia was 400 m^3/s in the summer (Mamo et al., 2019), a much higher value than that measured in the studied creek.

Petroleum hydrocarbons are formed by the chemical combination of hydrogen and carbons leading to a complex compound which, sometimes, contain impurities such as oxygen, sulphur, and nitrogen (Aminzadeh and Dasgupta, 2013). These combinations may form petroleum products such as light and heavy oils, dry gas and wet gas and they can be used for internal combustion engines and cooking gas (Aminzadeh and Dasgupta, 2013). The most common contaminants in the environment are petroleum hydrocarbons; the most often released hydrocarbons from crude oil and liquid petroleum products are the lighter fractions which are volatile (Cozzarelli and Baehr, 2003). Low molecular weight hydrocarbons ($C_8 – C_{10}$) were not detected in either surface water or sediment along the creek; this could be due to their higher solubility and bioavailability (Kuppusamy et al., 2020b). Studies have recorded that trend of hydrocarbon susceptibility to microbial degradation is as follows: linear alkanes > branched alkanes > small aromatics > cyclic aromatics (Brooijmans et al., 2009; Leahy and Colwell, 1990). In the bioremediation of Exxon Valdez oil spills, it was recorded that light molecular weight hydrocarbons (alkanes) are easily depleted (Atlas and Bragg, 2009).

In Ikolo Creek, Bayelsa State Nigeria, TPH concentrations recorded lower concentrations than those measured in Woji Creek; concentrations in surface water and sediment ranged from 0.001 to 0.437 mg/L and 0.001–0.44 mg/kg respectively (Ighariemu et al., 2019). TPH

Table 4. Ecological hazard quotient of petroleum hydrocarbons in surface water and sediment.

Compound	Surface water (HQ)					Sediment (HQ)				
	St1	St2	St3	St4	St5	St1	St2	St3	St4	St5
C_8	-	-	-	-	-	-	-	-	-	-
C_9	-	-	-	-	-	-	-	-	-	-
C_{10}	-	-	-	-	-	-	-	-	-	-
C_{11}	-	-	-	-	-	-	-	-	-	-
C_{12}	-	-	-	-	-	-	-	-	-	-
C_{13}	-	-	-	-	-	-	-	-	-	-
C_{14}	-	-	0.08	0.1	-	3.30E-02	-	2.70E-02	-	1.10E-02
C_{15}	-	-	0.11	0.22	-	3.70E-02	1.40E-02	3.40E-02	2.10E-02	2.30E-02
C_{16}	0.09	0.06	0.11	0.34	0.06	4.10E-02	1.60E-02	3.80E-02	3.80E-02	3.50E-02
C_{17}	0.09	0.07	0.11	0.42	0.06	4.90E-02	1.70E-02	4.50E-02	3.10E-02	2.60E-02
Pr	-	-	0.07	0.29	-	2.10E-02	8.50E-03	1.40E-02	9.20E-03	2.80E-02
C_{18}	0.11	0.08	0.18	0.46	0.07	6.70E-02	2.70E-02	5.40E-02	7.00E-03	2.70E-02
Ph	-	-	0.06	0.1	-	6.00E-03	-	3.80E-03	2.60E-02	8.10E-03
C_{19}	0.14	0.09	0.37	0.47	0.08	4.10E-02	1.70E-02	3.60E-02	2.40E-02	2.20E-02
C_{20}	0.15	0.11	0.47	0.45	0.09	4.20E-02	1.60E-02	3.70E-02	2.60E-02	1.80E-02
C_{21}	0.16	0.11	0.46	0.42	0.1	4.50E-02	1.80E-02	4.10E-02	2.80E-02	2.00E-02
C_{22}	0.17	0.12	0.43	0.39	0.11	5.10E-02	1.90E-02	4.60E-02	3.10E-02	2.30E-02
C_{23}	0.16	0.12	0.35	0.35	0.12	5.50E-02	2.00E-02	4.90E-02	3.30E-02	2.50E-02
C_{24}	0.18	0.12	0.22	0.31	0.12	4.70E-02	2.20E-02	4.40E-02	3.10E-02	2.90E-02
C_{25}	0.17	0.12	0.14	0.28	0.13	5.30E-02	2.60E-02	4.80E-02	3.40E-02	3.80E-02
C_{26}	-	-	-	-	-	5.10E-02	2.20E-02	4.70E-02	4.00E-02	2.90E-02
C_{27}	-	-	-	-	-	7.40E-02	2.30E-02	6.50E-02	4.20E-02	3.10E-02
C_{28}	-	-	-	-	-	5.90E-02	2.20E-02	5.30E-02	3.60E-02	2.90E-02
C_{29}	-	-	-	-	-	6.40E-02	2.30E-02	5.80E-02	3.60E-02	2.50E-02
C_{30}	-	-	-	-	-	5.30E-02	2.30E-02	4.40E-02	2.80E-02	7.50E-02
C_{31}	-	-	-	-	-	3.90E-02	9.80E-03	3.20E-02	2.10E-02	5.90E-02
C_{32}	-	-	-	-	-	1.50E-02	6.50E-03	1.30E-02	8.60E-03	1.00E-02
C_{33}	-	-	-	-	-	1.20E-02	3.20E-03	6.70E-03	4.80E-03	6.90E-03
C_{34}	-	-	-	-	-	1.40E-02	1.90E-03	5.70E-03	2.40E-03	6.30E-03
C_{35}	-	-	-	-	-	2.50E-02	-	2.90E-02	1.50E-03	1.40E-02
C_{36}	-	-	-	-	-	1.50E-03	-	7.20E-04	6.10E-04	7.20E-03
C_{37}	-	-	-	-	-	-	-	-	-	-
C_{38}	-	-	-	-	-	-	-	-	-	-
HI	1.42	1.01	3.15	4.59	0.94	0.99	0.36	0.87	0.56	0.62

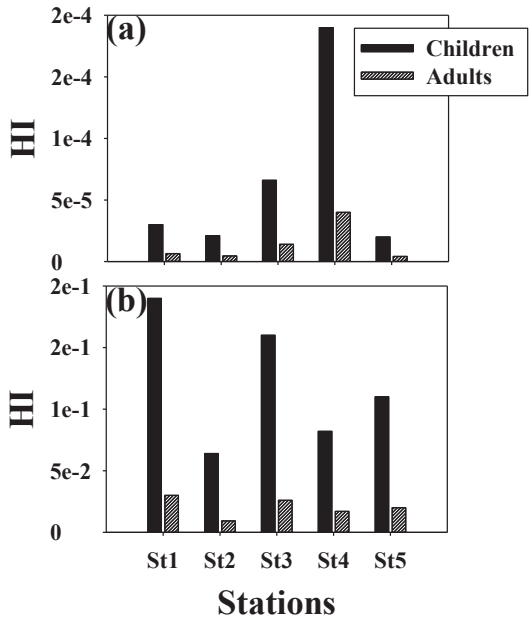

Figure 5. Hazard index (HI) estimated for human health risk due to ingestion of (a) surface water and (b) sediment.

concentrations in surface water of Algoa Bay, Eastern Cape, South Africa, which varied from 45.07 to 307 μg/L, were lower than those of Woji Creek, however, TPH in sediment (ranging from 0.72 to 27.03 mg/kg) was within the range measured in the present study (Adeniji et al., 2017a, b). Sediment sampled from River Nun, Amasoma Axises, Niger Delta, Nigeria had TPH concentrations ranging from 0.21 – 0.36 mg/kg, lower than those detected in Woji Creek (Alagoa et al., 2018). The highest concentration of petroleum hydrocarbons in sediment samples from the Bay of Fundy between Canada's Nova Scotia and New Brunswick provinces with hydrocarbons C_{16} to C_{35} (25 mg/kg) was higher than those measured along Woji Creek (Yang et al., 2018).

Petroleum hydrocarbons systematically pass through processes such as evaporation, dissolution, dispersion, photo-oxidation, and biodegradation when they are spilt into the aquatic environment, at different rates depending on the carbon makeup (Clement, 2018; Gray et al., 2010; Zeneli et al., 2019). This accounts for the difference in the hydrocarbon groups identified in surface water across the stations. Spatial distribution of petroleum hydrocarbons in surface water indicates that the site of origin of the petroleum hydrocarbons is between St3 and St4 since samples collected from these stations contain Pr and Ph; as a consequence of tidal flow, the hydrocarbons move upstream towards St2 and St1 and downstream towards St5 (Romero et al., 2017; Valentine et al., 2014; Yan et al., 2016). The concentration of TPH in surface water sampled from Qua-Iboe River, Ibeno, Akwa-Ibom State, Nigeria, ranged from 90 to 250 μg/l (Inyang et al., 2019), this was less than the concentration measured across Woji creek.

In the marine environment, the presence of aliphatic hydrocarbons can be due to natural source input such as pyrolysis (thermal decomposition of organic waste (Baskar et al., 2019)), diagenesis (the physical and chemical processes that affect materials after deposition, that enter into the marine ecosystem and sediments, i.e. the total processes that affect very young rocks, changes in composition, mineralogy or texture (Patterson and Runnells, 2003)). Others are biosynthesis (transformation of marine biotic organisms to hydrocarbons (Liu and Li, 2020; Wackett and Wilmot, 2015)). Anthropogenic processes such as urban waste, oil plants and refineries, oil waste, combustion of fossil compounds, industrial activities, etc. can also contribute to hydrocarbons in marine environment (Srivastava et al., 2019). Although St4 also indicates the influence of natural input of hydrocarbon, there is a consistent and clear indication of a strong influence of petrogenic source input in the creek. This is in agreement with a study carried out by Ihunwo et al. (2019) which identified the source of PAH in this creek as petroleum in nature.

Unresolved Complex Mixture (UCM) is used to identify the presence of marine (fossil) fuel hydrocarbon in aquatic samples (Farrington and Quinn, 2015). A higher proportion of $C_{23} – C_{33}$ is indicative of petrogenic sources, while a higher proportion of $C_{15} – C_{20}$ is indicative of marine biogenic sources. In the surface water samples, except for St4, all stations had a higher proportion of $C_{23} – C_{33}$ compared to $C_{15} – C_{20}$. Similarly, in the sediment, all stations also had higher values of $C_{23} – C_{33}$. This indicates that the source of hydrocarbons in the sediment and surface water were petrogenic.

According to Meyers (2003) and Kanzari et al. (2012) if the ratios of low molecular weight to high molecular weight (LMW/HMW) is less or close to 1 it is indicative of a biogenic input, however, if the ratio is >2 it is indicative of a fresh oil input (Ekpo et al., 2012). LMW = $C_{14} + C_{15} \ldots + C_{20}$ while HMW = $C_{21} + C_{22} \ldots + C_{34}$) (Ratheesh Kumar et al., 2019). In the surface water, LMW/HMW ratio was >2 across the creek, however, in the sediment, LMW/HMW at St2 and St4 was ≈2, and at St1, St3 and St5 the ratio value was close to 1. This indicates a possibility of both biogenic and petrogenic source of hydrocarbons in the sediment,

Table 5. Linear r (Pearson) correlation.

	TPH-Wat	TPH-Sed	EC-Wat	Temp-Wat	DO-Wat	pH-Wat	ORP-Wat	TDS-Wat	Depth-Wat	Width-Wat	Volume	Flowrate	pH-Sed	EC-Sed	ORP-Sed
TPH-Wat															
TPH-Sed	0.28														
EC-Wat	0.55*	0.42													
Temp-Wat	0.54*	0.54*	0.79**												
DO-Wat	-0.48*	-0.48*	-0.60**	-0.80**											
pH-Wat	0.27	-0.44	0.15	0.17	-0.10										
ORP-Wat	0.11	0.12	0.04	-0.22	0.34	-0.20									
TDS-Wat	0.53*	0.40	0.94**	0.85**	-0.63**	0.08	0.05								
Depth-Wat	-0.13	0.09	-0.01	-0.03	0.38	0.01	0.19	0.03							
Width-Wat	-0.23	0.19	0.27	-0.11	0.40	-0.29	0.66**	0.22	0.36						
Volume	-0.22	0.18	0.18	-0.09	0.48*	-0.19	0.56*	0.16	0.76**	0.88**					
Flowrate	-0.24	0.04	0.13	-0.20	0.57*	-0.14	0.61**	0.11	0.70**	0.89**	0.98**				
pH-Sed	0.41	-0.39	0.22	0.07	-0.31	0.52*	0	0.18	-0.64**	-0.34	-0.56*	-0.45			
EC-Sed	0.24	-0.20	0.42	0.01	0.23	0.32	0.68**	0.38	0.30	0.60*	0.57*	0.65**	0.33		
ORP-Sed	-0.04	0.27	0.19	0.03	0.35	-0.04	0.68**	0.19	0.69**	0.75**	0.88**	0.85**	-0.45	0.61**	

Asterix represents statistically significant difference, $p < 0.05$ - *, $p < 0.001$ - **.

however, the major source in the surface water is petrogenic. In a study carried out on sediment sampled from Forcados River, LMW/HMMW ratio was >1 at Abare, Sagbama, Bomadi, Oboro, Osain, Ogulaha and Yobebe, however, the ratio was <1 at Trofani and Abomobebe (Iwegbue et al., 2016). Hence, indicating a combination of sources along the river, but majorly petrogenic due to petroleum exploration in the area.

Carbon preference indices (CPI) was developed by (Bray and Evans, 1961) and it is the ratio of the odd number carbons ($C_{13} + C_{15} + C_{17} + \ldots C_{35}$) to even number carbons ($C_{12} + C_{14} + C_{16} + \ldots C_{36}$). CPI ≈1 indicates a petrogenic source of petroleum hydrocarbons in the sample. In the study river, CPI was ≈1 in all surface water and sediment samples indicating a petrogenic source of hydrocarbons in both mediums. According to Iwegbue et al. (2016), along Forcados River, CPI of sediment samples from Abare indicated that hydrocarbon originated from crude oil. While samples from Trofani, Abomobebe, Sagbama, Oboro and Ogulaha had values ≈1 indicates a petrogenic source of petroleum hydrocarbons, which were similar to results obtained from surface water and sediment samples across the studied creek.

According to Bourbonniere and Meyers (1996), ratios of terrigenous ($C_{27} + C_{29} + C_{31}$) to aquatic ($C_{15} + C_{17} + C_{19}$) n-alkanes (TAR) helps to distinguish allochthonous and autochthonous. Values of TAR greater than 1 indicates more watershed (allochthonous) source of hydrocarbon. Along the creek, TAR values varied in the surface water from >1 at St1, St2 and St5 to <1 at St2 and St3; in the sediment, St1 – St4 indicated allochthonous source input with values of TAR >1. Similarly, most stations with anthropogenic input of hydrocarbons sampled along the Segara Anakan Nature Reserve had TAR >1 (Dhamar et al., 2013). Sediment samples collected from the Cochin estuary in the Southwest of India also had TAR values >1 for all stations studied (Ratheesh Kumar et al., 2019).

Furthermore, C_{17}/Pristane and C_{18}/Phytane ratios are usually applied in the evaluation of the presence of oil and the relative biodegradation; for both ratios, values >1 indicate a petrogenic source of hydrocarbon but a value ≈1 indicates terrigenous/marine organic matter (Hidrokarbon et al., 2016). At St3 and St4 in surface water, both ratios showed values >1, confirming a petrogenic source of hydrocarbons in the surface water. In the sediment samples, C_{17}/Pr values indicate a petrogenic source at St1, St3 and St4, while C_{18}/Ph values indicate a petrogenic source at St1 and St3. Similar to these results, aliphatic hydrocarbons analysed in sediment sampled from Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina) had C_{17}/Pristane and C_{18}/Phytane ratio values >1 indicating petrogenic source due to the anthropogenic activities taking place along the bay (Commendatore et al., 2012). Similarly, sediment sampled from stations near harbours and waste discharge outfall of the refinery site along with Segara Anakan Nature Reserve, Indonesia had values of both ratios >1 (Dhamar et al., 2013).

ERA indicate medium to high risk across the creek in surface water and sediment. Surface water samples collected from all stations had HI > 1, however, sediment indicated medium risk (0.1 = HI < 1) (Table 4). The ecological effect of petroleum in fluvial systems could range from habitat disruption to effects on specific species including biosynthetic, energetic, developmental, and reproductive disruption (McDowell Capuzzo et al., 1988). In freshwater, high molecular weight hydrocarbons can negatively affect macroinvertebrates assemblage (Anson et al., 2008). Aquatic invertebrates living in intertidal zones such as Woji Creek and the numerous organisms that make up their habitat are at risk due to the constant inflow of contaminants that wash over them (Elmgren et al., 1973). According to results obtained by Yeung et al. (2020), petroleum hydrocarbon concentrations of ≥1.45 mg/L showed growth inhibition of two microalga species (Isochrysis galbana and Chaetoceros gracilis) and acute mortality in three marine animals (Tigriopus japonicus, Artemia franciscana and Oryzias melastigma). Petroleum spill on surface water can also lead to a hypoxic condition by interrupting the equilibrium that exists between marine habitat and the atmosphere (air-saturated; normoxic) (Davenport, 2001).

Petroleum hydrocarbons are more lipophilic than they are hydrophilic with exception of the highly viscous products such as tar and motor oil (Das and Chandran, 2011; National Research Council (US), 2003); petroleum hydrocarbons are highly volatile and are easily inhaled and absorbed by the lungs (Gupta, 2016; Wismer, 2016). Petroleum hydrocarbons with lower molecular weight (LMW) such as gasoline, are absorbed from the gastrointestinal tract (Dalefield, 2017). Aliphatic hydrocarbons have been associated with accidental poisoning among children; it is reported that 28,000 children younger than 5 years ingest petroleum distillates accounting for 12–25 % of deaths in the age group (Gupta, 2016). Hazard Index for accidental ingestions of sediment was and surface water were both <1 for children and adults indicating no risk to human beings in the creek. However, their lipophilicity may promote bioaccumulation in the human body (Almeda et al., 2013; Chase et al., 2013; Muijs and Jonker, 2010). Studies have recorded that petroleum hydrocarbons can lead to systematic damage in organs (Chiesa et al., 2019; Demirtepe et al., 2019; Tsiaoussis et al., 2019; Zhang et al., 2019) When accidently ingested or inhaled, LMW hydrocarbons can spread through the pulmonary tree, resulting in fulminating pulmonary oedema and bronchopneumonia (Calello, 2007); they can also lead to depression of the central nervous system and also damage the liver, kidneys, and bone marrow (Gupta, 2016; Lee and Bye, 2019).

Correlations between physicochemical parameters, river hydrolology and TPH in surface water and sediment are presented in Table 5. The DO displayed a negative correlation with hydrocarbons concentration in the sediment and surface water (r = -0.48* – Surface water, r = -0.48* – Sediment). This was similar to studies carried out in the Buffalo River Estuary in the Eastern Cape Province, South Africa (Adeniji et al., 2017a, b). The negative correlation observed between DO and petroleum hydrocarbons confirms pollution in aquatic systems due to petroleum hydrocarbons usually leading to anoxic/hypoxic condition (Akinola et al., 2019). The DO in surface water showed a negative correlation with pH in surface water (r = -0.10) and sediment (r = -0.31), this trend is supported by other studies (EPA, 2001; Omer, 2019; Tajmunnaher and Chowdhury, 2017). However, DO showed a strong correlation with ORP in sediment (r = 0.35), depth (r = 0.38), width (r = 0.40), volume (r = 0.48*), and flow rate (r = 0.57*). Hydrocarbon input negatively affects the quantity of oxygen that can dissolve in the aquatic system, thereby creating an anoxic condition for aquatic biota (Peirce et al., 1998; Muralikrishna and Manickam, 2017), hence the negative correlation observed between DO and TPH in both mediums. DO and temperature shows strong negatively correlated (r = -0.80*); confirming that dissolved oxygen in the surface water is higher at lower temperature and vice versa (Sheldon et al., 2019).

Chemical pollutants can change pH levels and increase water toxicity (Atta, 2020). The pH in both surface water showed a positive correlation with TPH in surface water (r = 0.27) and a negative correlation with TPH in sediment (r = -0.44). The ORP in the surface water showed a positive correlation with TPH in surface water (r = 0.11) and sediment (r = 0.12). Although the EC in the surface water showed a positive correlation with TPH in sediment (r = 0.42), it showed a statistically significant correlation with TPH in surface water (r = 0.55*); this trend was not similar to EC in the sediment (TPH – Water: r = 0.24, TPH - Sediment: r = -0.20). The TDS showed positive correlation with hydrocarbons in the surface water (r = 0.53*) and sediment (r = -0.40). Similar to this study, the study of Adeniji et al. (2019) in Kidd's Beach (Cape Province) in South Africa found a positive correlation between the TDS and EC. The negative correlation observed shows that, despite the increasing trend of TDS and EC downstream, TPH is reducing downstream.

5. Conclusion

Illegal transportation of petroleum products along the creek can lead to periodic spill, and this possess ecological threat to surface water and benthic organisms. The assessment of total petroleum hydrocarbons in surface water and sediment along Woji Creek in the Niger Delta Estuary, Nigeria showed higher concentrations of hydrocarbons in the sediment compared to the surface water. The hydrocarbons measured in the creek was confirmed to be from petrogenic sources. Potential ecological risk assessment of the detected hydrocarbons in the system indicates risk in the surface water. However, no risk was measured for human health due to human ingestion of sediment or surface water. Thus, the present study confirmed that the illegal transportation of petroleum products along this creek which leads to periodic spill poses ecological threat to surface water organisms.

Declarations

Author contribution statement

Owhonda Chikeru Ihunwo: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mark Obinna Onyema: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Vremudia Onyeajoma Wekpe: Conceived and designed the experiments; Analyzed and interpreted the data.

Christopher Okocha: Analyzed and interpreted the data.

Amir Reza Shahabinia, Prince Chinedu Mmom, Amalo Ndu Dibofori-Orji, Estefanía Bonnail: Contributed reagents, materials, analysis tools or data.

Lebechi Emmanuel, Vincent N. Okwe, Chimdi B. Lawson: Performed the experiments.

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Data availability statement

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Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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