



Seasonal Variation in Petroleum Hydrocarbon Concentrations in Surface Water, Sediment, Crab (*Callinectes sapidus*), and Periwinkle (*Tympanotonus fuscatus*) from the New Calabar River, Nigeria

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Abstract

The New Calabar River is increasingly threatened by pollution resulting from treated and untreated effluents discharged from oil exploration activities and other anthropogenic sources. The research evaluated the effect of seasonal variation on hydrocarbon contamination in the New Calabar River using surface water, crab (*Callinectes sapidus*), and periwinkle (*Tympanotonus fuscatus*) as environmental indicators. Samples were collected during both dry and wet seasons from five sampling locations: Choba (SP-A), Mgbuodohia (SP-B), Ogbogoro (SP-C), Rumuolumeni (SP-D), and Rumuokparali (SP-E). Standard analytical procedures were employed to determine the concentration of Total Petroleum Hydrocarbon (TPH). Sample preparation involved solvent extraction and silica/alumina or Florisil column chromatography, while analyses were conducted using Gas Chromatography with Flame Ionization Detection (GC-FID). Sediment and biological samples were analyzed using HNO₃ and H₂SO₄ acid in the ratio of 3:1 prior to analysis. Detectable concentrations (Mg/L) of hydrocarbon (TPH) in surface water were in the following range: the dry season values were (0.08 - 0.79) and (0.05 - 0.72) in the wet season. The results (Mg/Kg) of hydrocarbon (TPH) in sediment ranged between (0.12 - 0.95) in the dry season and (0.05 - 0.09) in the wet season. The results of the concentrations (Mg/Kg) of hydrocarbon content (TPH) in the blue crab and periwinkle recorded dry season values (0.01 - 0.02) and (ND - 0.01) in the wet season. The result revealed seasonal variation in hydrocarbon concentrations across all environmental matrices, with generally higher concentrations observed during the dry season compared to the wet season. Surface water and sediment contained measurable concentrations of TPH, while blue crab and periwinkle accumulated detectable levels of hydrocarbon, indicating bioaccumulation within the aquatic ecosystem. Although the concentrations recorded were generally within Standard Organization of Nigeria (SON 2017) acceptable limits, the presence of hydrocarbons reflects continuous anthropogenic inputs into the river. The study concludes that seasonal changes significantly influences hydrocarbon distribution in New Calabar River and therefore, emphasizes the need for adequate and continuous environmental monitoring and stricter regulation of industrial effluent discharge to safeguard aquatic ecosystem and public health of New Calabar River should be implemented to mitigate increased anthropogenic heavy metal inputs into the river.

Keywords: Contamination, Surface Water, (Blue Crab-*Callinectes Sapidus*), (Periwinkle-*Tympanotonus Fuscatus*), and Hydrocarbon concentrations

Introduction

Water is the most valuable natural resources available to man, without which no life can survive. Therefore, adequate and safe water supply is a pre-requisite for significant socio-economic development of any community (Akpan-Idot et al., 2012). Water is considered to be an essential requirement for human and industrial growth. The

physical and chemical properties of water greatly influence its uses, distribution and richness of the biota (Unanom & Apkan 2010; Courtney & Clement, 2011). A major component for survival of life on earth is water and it contains minerals, essential for humans, for world and as well as aquatic organisms. Lakes reservoirs and surface water are most important to plant's freshwater resources and provide innumerable benefits. They are well used for irrigation and domestic purposes and provide an ecosystem for aquatic life, especially fish, thereby functioning as a source for essential protein and for significant elements of the world's biological diversity. Their economic and social benefits are of great essence as a result of recreation and tourism and are aesthetically and culturally relevant for people through the world Anani et al. (2018). The term used to describe a large family of several hundred chemical compounds that originally come from crude oil is referred to as Total petroleum hydrocarbon (TPH). Petroleum products are made from crude oil, which can contaminate the environment. Crude oil measures so many different chemicals in it and in other petroleum products; therefore, it is not practical to measure each one separately. However, it is relevant to measure the total amount of TPH at a site. Total petroleum hydrocarbon is a mixture of chemicals, but they are all built up mainly from hydrogen and carbon, called hydrocarbons. TPH are divided into groups of petroleum hydrocarbons by Scientists. They act alike in soil or water. These groups are called petroleum hydrocarbon fractions. Each fraction contains many individual chemicals. TPH contains some chemicals that may be found in hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorine, as well as other petroleum products and gasoline components. However, it is likely that samples of TPH will contain only some or a mixture of these chemicals. United States Environmental Protection Agency (EPA, 2011). TPH is a commonly used gross parameter for quantifying environmental contamination originated by various petroleum hydrocarbon content (PHC) products such as fuel, oils, lubricants, waxes and others, Environmental Sciences Division (ESD, 2017).

The availability of water is limited by contamination of this important resource, with an attendant possibility of causing human and wildlife health problems, reduced biodiversity, poverty, environmental hunger and degradation, amongst others. Total Petroleum Hydrocarbons are regarded as conventional petroleum contaminants that have been recognized and monitored for decades, particularly in areas affected by oil exploration, refining, transportation, and spills. Although they are classified as emerging micro pollutants, they remain a significant threat to water quality, sediment quality, and aquatic organisms due to their persistence and toxicity. The introduction of high concentrations of the activities of these chemicals into the environment is still taking place. A large number of people are, however, not aware of the implications of living with the presence of these chemicals in the environment. There is therefore the need for the appropriate measures to be considered in order to control these activities in Nigeria (Eneh, 2011).

Ten footed crustaceans belonging to the order Decapoda, are known as Crabs, they are in the infra order brachyuran and are generally shielded with a thick exoskeleton and a single pair of pincers. They are majorly semi-terrestrial and aquatic organisms often found in brackish water, swamps, sand shores, freshwater, and oceans with a typical life span between three and four years depending on the species, they are regarded as marine inhabiting the littoral, superlittoral and even up shore zones. Most of the crab species are usually sexual dimorphic, with males having a narrow 'V-shaped' abdomen, and in addition to larger pincers and claws which are used for communication, attracting a mate and warding off intruders (How et al., 2015). They are omnivores, mostly feeding on algae, crustaceans, fungi, bacteria, detritus, and other food sources depending on the species (Edema et al., 2015). Despite its importance as an animal protein source and medicinal benefits, there is paucity and knowledge gap on its harvesting, trade, farming, and biology in the southern part of Nigeria. Crabs are consumed as food in many countries and are part of the basic components of the ecosystem. More than 100 species of crabs are recognized worldwide, with nine species common to West African countries, including Nigeria. Crabs mostly occur at the mouth of estuaries and along the course of many rivers. They constitute a nuisance by damaging set nets in the water feeds on fish, aquatic vegetation, mollusks, crustaceans, and annelids. They also serve as prey to mammals, birds and fishes but they constitute one of the most vital members of the estuaries food chain Hallett et al. (2013). They are dominant in many estuaries habitats where salinity and temperatures can fluctuate dramatically daily and have been found at 580 to 6000m to seas shore. They also increase the breakdown of decaying organic matter into smaller inorganic forms such as nitrates and phosphates. The blue crab is an inshore estuaries crab species which dwell near the bottom of the water bodies and occupies a variety of aquatic habitats from the lower reaches of freshwater rivers; estuaries to coastal marine waters are highly mobile, making it very easy for them to move between areas and select habitats. They live on muddy bottoms in mangrove areas and river mouths. Crab levels make up 20% of all marine

crustaceans caught and farmed worldwide, with over 1.5 million tonnes being consumed annually. The highly sought-after shellfish is the blue crab and is caught by both recreational and commercial fishermen. Its scientific name is *Callinectes sapidus*. It means “beautiful savory swimmer translated from Latin. The blue crab is also known as Hard – shells (not molting), Peelers (about to molt), Busters (started to molt), Soft – shells (just molted, not yet hard), Jimmies (adult males), Sooks (adult females), She- crabs or Sallies (immature females), Sponges/Sponge crabs (females crying eggs). Its life span is about 3 to 4 years, length is up to 9 inches across the carapace/shell, and its weight is approximately $\frac{1}{3}$ pound at maturity (Miller, 2011). Blue crabs are the most valuable fishery in the Chesapeake Bay. They are also major predators of benthic communities and are prey for many other fish species. Blue crabs are bottom- dwellers that use beds of submerged aquatic greases as sources of food, nursery habitat for young, and shelter during mating and molting. Blue crab distribution varies with age, sex, and season. They tend to be abundant in shallow-water areas during warm weather (Rains, 2014). As the water temperature drops each year, they burrow into sediment in the deeper parts of the Bay for the winter. The blue crab uses multiple habitats in the Chesapeake Bay throughout its life. Blue crab habitats include underwater grasses and oyster reefs, and they range from shallow, brackish waters to deeper, saltier waters. Blue crabs eats almost anything, including oyster, clams, smaller crustaceans, mussels, freshly dead fish, plant and animal detritus- and smaller and soft- shelled blue crabs. To mate, a male crab cradles a female crab in a pose known as “doubler” for a few days before the female’s terminal molt. They stay with her after mating until her shell hardens and to ensure another male doesn’t mate with her. Blue crabs have an “apron” that covers their abdomen. Males’ aprons are thin; females’ are wider (Ralph et al., 2014). In the Chesapeake Bay, people often refer to males’ aprons as looking like the Washington Monument while females’ aprons look like the Capitol dome. Blue crab claws are bright blue, and mature females have red tips on their claws too. The blue crab’s shell, called the “carapace,” is blue to olive green. They have three pairs of walking legs and rear swimming legs that look like paddles. They reach maturity in 12 to 18 months. Growth rates are affected by water temperature. In the Chesapeake Bay, blue crabs mate and spawn from spring to fall. Females migrate to the mouth of the Bay to spawn and can produce between 750,000 and 3, 200,000 eggs per brood. They grow more quickly in warm water (Ogburn et al., 2014).

The common periwinkle or winkle (*Tympanotonus fuscatus*) is a species of small edible whelk or sea snail, a marine gastropod mollusk that has gills and an operculum (Reid et al., 2011). It has been known as a robust intertidal species with a dark and sometimes banded shell. It is native to the rocky shores of the northeastern Atlantic Ocean and introduced to the northwestern Atlantic Ocean. The shell contains six to seven whorls with some fine threads and winkles and also the shell is broadly ovate, thick, and sharply pointed except when eroded (Benson et al., 2011). The color varies from grayish to gray-brown, often with dark spiral bands. The base of the columella is white. The shell lacks an umbilicus. The white outer lip is sometimes checked with brown patches. The inside of the shell is chocolate (Benson et al., 2011). The width of the shell ranges from 10 to 12 millimeters (0.39 to 0.47 in) at maturity (National Park Services, 2016), with an average length of 16 to 38 millimeters (0.63 to 1.50 n) (Benson et al., 2011). The common periwinkle is mainly found on rocky shores in the higher and middle intertidal zones (Benson, 2008). It sometimes lives in small tide pools. It may also be found in muddy habitats such as estuaries and can reach depths of 180 feet (55 m) (Benson, 2008). When exposed to either extreme cold or heat while climbing, a periwinkle will withdraw into its shell and start rolling, which may allow it to fall to the water. *Tympanotonus fuscatus* is an omnivorous, grazing intertidal gastropod (Chang et al., 2011). The female specimens have been observed to be ripe from February until the end of May, when most are spawning. Male specimens are mainly ripe from January until the end of May and lose weight after copulation. The common periwinkle can act as a host for various parasites, including *Renicola roscovita*, *Cryptocotyle lingua*, *Microphallus pygmaeus* and *Himasthla* sp. Periwinkles are considered a delicacy in African and Asian cuisines. The meat is high in protein, omega -3 fatty acids, and low in fat; according to the USDA National Nutrient Database for Standard Reference, raw snails in general are about 80 % water, 15 % protein, and 1.4 % fat. In the seafood supply chain in general, the supply chain consists of a collector, processor, distributor, and finally the retailer. Periwinkles are graded by number of snails per kilogram. The common periwinkle can usually be stored in the fridge for up to a week, but this may vary depending on how long they have been stored prior to sale, and how they have been kept since the moment they are fished. As long as they are kept moist and cold, they can survive well for a longer time. It is not recommended to store at temperatures below zero degrees Celsius, even if research has shown a Median Lower Lethal Temperature of -13.0 degrees Celsius (Daveport, 2005). Although common periwinkle may survive when put back into seawater, they seem to be unable to move and climb. This research work was therefore performed to assess the seasonal variation of

hydrocarbon contamination in surface water, sediment, blue crab, (*Callinectes sapidus*) and periwinkle (*Tympanotonus fuscatus*) collected from selected locations along the Akpor axis of the New Calabar River.

Materials and Methods

The New Calabar River is bordered at longitude $7^{\circ}60'E$ and latitude $5^{\circ}45'N$ in the coastal region of Rivers State, Niger Delta, Nigeria. The river releases its water to the Atlantic Ocean. The Rumuolumeni/Akpor area where the river cut across is one of the industrial hubs of the state and comes next to Trans Amadi Industrial Layout. Industries situated along its bank discharge their effluent into it. Surface runoff from soil erosion and lumbering activities may lead to widespread contamination of the river. The river is under forest operations (transportation of logs of wood) and constant dredging, sea transportation, among other anthropogenic activities taking place within the river. There is a recent addition of illegal oil bunkering activities in the river (Dienye & Woke 2015). New Calabar River receives fresh water, industrial effluent, and domestic water from waterfront settlements and communities along the river (Kpee, 2012). Industries and companies that indulge in the discharge of wastes into New Calabar River include, among others, Indomie, Eagle Cement, Agip Oil, Wilbros Nigeria, etc.

The study area is in Obio/Akpor Local Government Area in the metropolis of Port Harcourt. It is one of the major centers of economic activities in Nigeria, and one of the major cities of the Niger Delta, located in Rivers State. It is popularly known as Gateway Local Government Area because of its location. It has a land mass of approximately 311.71 square kilometers and is accessible by road, sea, and air transportation. Obio- Akpor was created on the 3rd of May 1989. The local government area covers 260km². The 2006 Census recorded a population of 464,789. Its postal code or ZIP code is 500102. Obio/Akpor has its headquarters at Rumuodomaya. The original indigenous occupants of the area are the Ikwerre people (Obio/Akpor is constituted mainly by people of Ikwerre ethnic nationality). Specifically, there are four (4) prominent kingdoms that constitute the Local Government Areas, which are: Akpor, Apará, Evo and Rumueme kingdoms. It also has an average of 2.82% growth rate which puts the population of the Local Government Area as at 2004 to be over 500,000 people (National Bureau of Statistics, 2004). A sub-group of Igbo people are also its occupants. The Local Government Area is rich with land and natural resources, such as land, soil, vegetation, water, coal, petroleum, gas, animals, wildlife, air, wind and atmosphere, clay, sand and gravel. Historically, Obio-Akpor people are descendants of Aro migrants who moved inland. Obio- Akpor is bounded by Port Harcourt (Local Government Area) to the south, Oyigbo and Eleme to the east, Ikwerre and Etche to the north, and Emohua to the west (Okoh, 2003).

Location and Delineation

The area belongs to the south-south region of Nigeria, also known as the Niger Delta region. It is located between the latitudes $4^{\circ}45'N$ and $4^{\circ}60'N$ and longitudes $6^{\circ}50'E$ and $8^{\circ}00'E$.

Climate and Other Environmental Conditions

The study area enjoys a tropical hot monsoon climate due to its latitudinal position. The tropical monsoon climate is characterized by heavy rainfall from April to October, ranging from 2000 to 2500 mm with high temperatures all year round and relatively constant humidity. Covering around 90 sq mi, Obio / Akpor is generally a lowland area with an average elevation between 20 and 30 meters above sea level. The geology comprises basically an alluvial sedimentary basin and basement complex (Eludoyin, 2010). The thick mangrove forest, raffia palms, and light rainforest are the major types of vegetation found in this area. Due to high rainfall experienced in the area, the soil in the area is usually sandy or sandy loam. It is always leached, underlain by a layer of impervious pan. The study area is well drained with both fresh and salt water. The salt water is caused by the intrusion of seawater inland, thereby making the water slightly salty. As resulting to continuous heavy rainfall and river flow, the study area experiences severe flooding almost every year.

The human activities and industrial operations that occur at the various study stations of this research work account for the reason for this investigation. People dwelling along the river are mostly farmers and fishermen whose activities contribute to a large extent to polluting the river. Industrial effluents are in most cases discharged directly into the river. A total of five different sampling sites were selected from the New Calabar River (NCR) within

Obio/Akpor Local Government Area; they include: Choba, Ogbogoro, Mgbuodohia, Rumuolumeni, and Rumuokparali, Rivers State, Nigeria. The sampling sites are coded and shown below.

Description of locations and their codes

Locations	Description
NCR	New Calabar River
SP-A	Choba
SP-B	Mgbuodohia
SP-C	Ogbogoro
SP-D	Rumuolumeni
SP-E	Rumuokparali

Experimental design

Surface Water Sampling

Surface Water samples were collected randomly at five different sampling points (10-25 cm) into sterile polyethylene glass bottles fitted and then closed underwater. The containers were prewashed with 20% analytical grade nitric acid and were rigorously rinsed with distilled deionized water prior to sampling. The containers were pre-rinsed again twice with the same water sample they are to contain before the sample was taken. The sample was collected below the surface film of the water. Samples were stored in an ice-chest container and transported to the laboratory for analysis. Water samples were preserved with analytical-grade nitric acid to give a pH < 2 to minimize precipitation and sorption losses to the container walls.

Sediment Sampling

Composite samples were collected during low tide at the five different sampling points (0-5 cm) depth using an American Public Health Association Standard (APHA 2011) by an Eckman grab sampler from 3 to 4 points at each location. The sediment was poured into pre-rinsed plastic bottles and appropriately labeled. The sediment was collected below the surface of the sediment using standard methods. Sediment samples were stored in an ice-chest box and transported to the laboratory for further analysis.

Biota Sampling

Biota (blue crab: *Callinectes sapidus* and periwinkle: *Tympanotonus fuscatus*) were hand-picked a few centimeters below the top of the sediment along with fresh water and washed with distilled water to remove soil and sediment before they were transferred into well-labeled aluminum foil containers. After collection, all the samples were stored in an ice-packed chest and transported to the laboratory. They were further refrigerated in the laboratory at 4 °C to inactivate microbes and to preserve the integrity of the samples prior to analysis.

Sample Preparation

Water sample Preparation

The surface water sample collected was pre-concentrated following a standard procedure described by Ramesh et al. (2001) and Essen et al. (2009). Two polyethylene bottles with snap caps were first treated with dilute HNO₃ and subsequently washed with a warm organic detergent dissolved in distilled water. Therefore, roughly 100 mL of water samples from each location (Choba), (Mgbuodohia), (Ogbogoro), (Rumuolumeni), (Rumuokparali) were filtered using a 0.2 µm filter to remove any suspended matter and then stored in prepared polyethylene bottles. After filtration, the filtrates were treated separately with concentrated HNO₃ to adjust their pH value to 4.00 ± 0.05 before they were buffered with 2 ML of 0.1M Potassium hydrogen phthalate of 1% (w/v), and methanol solution of sodium di-benzyl di-thiocarbonate was added to each filtrate; and the solutions were stirred intermittently for roughly 18-20 min. Each solution was eluted with 4 M HNO₃, and the acid elutes were stored for metal analysis.

Sediment Sample Preparation

Sediment samples were transported to the laboratory in ice-packed coolers and stored at 4°C to constant weight to minimize loss of volatile hydrocarbon, and homogenized by grinding with a porcelain mortar and pestle. The dried, homogenized samples were sieved through a 2 mm stainless steel mesh to remove debris, stone and shells. Approximately 10g of the sieved sediments was weighed into a clean glass beaker. Extraction was carried out using 50 ml of a 1:1 (v/v) mixture was centrifuged at 3000 rpm for 10 minutes and the supernatant decanted into a clean round-bottom flask. The extraction procedure was repeated twice and the extract was combined.

The combined extract was dried over anhydrous sodium sulfate and concentrated to approximately 2 ml using a rotary evaporator at 40°C. The concentrated extract was subjected to cleanup using florisil column chromatography following EPA method 3630C to remove co-extract polar and biogenic materials. The clean extract was then concentrated to 1 ml under a gentle stream of high-purity nitrogen and stored in amber vials at 4°C prior to TPH analysis.

Biota Sample Preparation

Samples of blue crab and periwinkle were thawed at room temperature and rinsed thoroughly with distilled water to remove adhering sediments, debris, and other external contaminants. The tissue of interest was carefully dissected using solvent-rinsed stainless-steel instruments to avoid contamination. The dissected tissue was then homogenized using a laboratory homogenizer to obtain a uniform and representative sample. The tissue was mixed with anhydrous sodium sulfate to remove residual moisture and produce a dry, free-flowing sample suitable for subsequent extraction. Finally, an accurate weigh portion approximately (10 – 20 g) of the prepared samples was transferred into a clean extraction vessel for Total Petroleum Hydrocarbon (TPH) analysis. The dried sample was extracted with a 1:1 (v/v) mixture of n-hexane and dichloromethane using the Soxhlet extraction technique, such as ultrasonic extraction or accelerated solvent extraction (ASE). Following extraction, the solvent extract was filtered through anhydrous sodium sulfate to remove remaining moisture and concentrated using a rotary evaporator or a gentle stream of high-purity nitrogen to a final volume of approximately 1-2 mL.

To eliminate co-extracted lipids and other biological interference, the concentrated extract was purified using a silica gel or Florisil column previously conditioned with n-hexane. The purified extract was collected, re-concentrated, and transferred into amber glass vials for instrument analysis.

Determination of Total Petroleum Hydrocarbon (TPH) in surface water, sediment and Biota

Total Petroleum Hydrocarbon (TPH) concentration in surface water, sediment, and biota samples were determined using Gas Chromatography equipped with a Flame Ionization Detector (GC-FID) Surface water samples were extracted by liquid-liquid extraction following U.S. EPA (1996) method 3510C using n-hexane. Sediment samples were extracted by ultrasonic extraction following U.S. EPA (2007) method 3550C, while biota samples (Blue crab- *Callinectes sapidu* and periwinkle *Tympanotonus fuscatus*) were homogenized extracted with a 1:1 (v/v) mixture of n-hexane and dichloromethane after appropriate sample preparation. All extracts were dried over anhydrous sodium sulfate, concentrated to ~ 1-2 ML using a rotary evaporator or under a gentle stream of nitrogen, and purified using silica gel or Florisil column chromatography following U.S. EPA (1996) method 3630C to remove co-extracted lipids and polar interferences. The purified extracts were transferred into clean amber glass vials and analyzed by GC-FID following the determinative procedures of EPA Method 8015D (U.S. EPA, 2003). Quantification of TPH was achieved by comparing the chromatographic peak areas of the samples with those of certified hydrocarbon calibration standards. Quality assurance and quality control procedures, including the analysis of reagent blanks, duplicate samples, calibration standards, and matrix spike recoveries, were employed throughout the analytical process to ensure the accuracy, precision, and reliability of the results.

Results

Results of the seasonal variation concentrations of Total Petroleum Hydrocarbons (TPH) in surface water, sediment and biota (Blue crab and Periwinkle) are presented in Tables 1-3

Table 1: Seasonal concentrations (mean±SD) of TPH in surface water samples from the studied locations (mg/L)

Locations	Wet Season	Dry Season
Sampling Identity	TPH	TPH
Choba	0.05±0.01	0.08±0.01
Mgbuodahia	0.34±0.03	0.44±0.03
Ogbogoro	0.25±0.01	0.28±0.01
Rumuolumeni	0.32±0.02	0.39±0.01
Rumuokparali	0.72±0.06	0.79±0.01

Total Petroleum Hydrocarbon (TPH) in the wet season varied between 0.05±0.01 for (SP-A), 0.34±0.03 for (SP-B), 0.25±0.01 for (S-C), 0.32±0.02 for (SP-D) and 0.72±0.06 for (SP-E). Choba (SP-A) recorded the lowest value while Rumuokparali (SP-E) recorded the highest value in both dry and wet seasons. The level of total petroleum hydrocarbons (TPH) in water was within Standard Organization of Nigeria (SON, 2017) Standards of 0.007 mg/l.

Table 2: Seasonal concentrations (mean±SD) of TPH in sediment samples from the studied locations (mg/L)

Locations	Wet Season	Dry Season
Sampling Identity	TPH	TPH
Choba	0.05±0.04	0.12±0.01
Mgbuodohia	0.09±0.08	0.63±0.10
Ogbogoro	0.07±0.05	0.89±0.16
Rumuolumeni	0.07±0.05	0.83±0.02
Rumuokparali	0.08±0.02	0.95±0.05

Total Petroleum Hydrocarbon (TPH) in the dry season occurred between 0.012±0.01 for (SP-A), 0.63±0.10 for (SP-B), 0.89±0.16 for (SP-C), 0.83±0.02 for (SP-D), and 0.95±0.05 for (SP-E). Choba (SP-A) recorded the lowest value while Rumuokparali (SP-E) recorded the highest value. TPH in the wet season varied between 0.05±0.04 for (SP-A), 0.15±0.06 for (SP-B), 0.10±0.01 for (SP-C), 0.16±0.04 for (SP-D) and 0.13±0.09 for (SP-E). Choba (SP-A) recorded the lowest value while Mgbuodohia (SP-B) recorded the highest value. The level of total Petroleum Hydrocarbons (TPH) in water was below Standard Organization of Nigeria (SON, 2017) drinking water limit of 0.007 mg/l and below USEPA (2009) and NIS (2006) effluent discharge limit of 0.5 – 1000 mg/l. The presence of TPH in river water is of concern to the public.

Table 3: Seasonal concentrations (mean±SD) of TPH in blue crab and Periwinkle samples from the studied locations (mg/L)

Locations	Sampling Identity	Wet Season	Dry Season
		TPH	TPH
Choba	Sea Blue Crab	ND	0.01±0.00
Mgbuodohia	Sea Blue Crab	ND	0.01±0.01
	Periwinkle	ND	0.02±0.01
Ogbogoro	Sea Blue Crab	0.01±0.00	0.01±0.01
	Periwinkle	0.01±0.00	0.01±0.01
Rumuolumeni	Sea Blue Crab	0.01±0.01	0.02±0.01
	Periwinkle	0.01±0.00	0.01±0.01

Rumuokparali	Sea Blue Crab	0.01±0.00	0.02±0.01
	Periwinkle	0.01±0.00	0.01±0.01

Total Petroleum Hydrocarbon (TPH) occurred between 0.01±0.00 – 0.02±0.01 in the dry season and ND - 0.02±0.01 in the wet season. SP-A (Choba) and SP-B (Mgbuodohia) were not detected (ND) in the wet season. All the sampled locations in the wet season recorded the same values whereas, the values varied in the dry season. The level of TPH was below standard Organization of Nigeria (SON, 2017) Standards of 0.007 mg/Kg.

Discussion

Total Petroleum Hydrocarbon (TPH) in Surface Water

Table 1: Presents the seasonal concentrations of Total Petroleum Hydrocarbons (TPH) in surface water collected from five sampling locations (Choba, Mgbuodohia, Ogbogoro, Rumuolumeni, and Rumuokparali) during the wet and dry seasons. The results are expressed as mean ± standard deviation (SD) in mg/L, where the mean represents the average concentration from replicate analyses, while the standard deviation indicates the degree of variation among the measurements. The relatively low SD values (±0.01–0.06) suggest good analytical precision and consistency of the measurements. The TPH concentrations during the wet season ranged from 0.05 ± 0.01 mg/L at Choba to 0.72 ± 0.06 mg/L at Rumuokparali. During the dry season, concentrations ranged from 0.08 ± 0.01 mg/L at Choba to 0.79 ± 0.01 mg/L at Rumuokparali. The data indicate that all sampling locations recorded higher TPH concentrations during the dry season than in the wet season. Among the locations, Rumuokparali consistently recorded the highest TPH concentrations in both seasons (0.72 ± 0.06 mg/L and 0.79 ± 0.01 mg/L), suggesting greater petroleum contamination in this area. This may be attributed to intensive anthropogenic activities such as petroleum exploration, oil transportation, illegal refining, urban runoff, industrial discharges, and heavy vehicular activities. The persistence of elevated TPH concentrations in both seasons indicates a continuous input of petroleum hydrocarbons into the aquatic environment.

Conversely, Choba recorded the lowest concentrations in both seasons (0.05 ± 0.01 mg/L and 0.08 ± 0.01 mg/L), suggesting relatively lower petroleum contamination. This may reflect reduced industrial activities, greater water exchange, or lower direct discharge of petroleum-related pollutants in the area. The observed seasonal variation demonstrates that TPH concentrations were generally higher during the dry season than during the wet season. This trend is commonly attributed to reduced water volume, limited dilution, increased evaporation, and lower river flow during the dry season, resulting in the concentration of pollutants in surface waters. During the wet season, rainfall increases water volume and enhances dilution, thereby reducing measured concentrations despite continued pollutant inputs. Although the differences between seasons appear moderate, the consistent increase in dry-season values across all locations indicates that seasonal hydrological conditions significantly influence petroleum hydrocarbon concentrations in the study area. Such seasonal variation has important ecological implications because prolonged exposure to elevated TPH levels may adversely affect aquatic organisms by reducing dissolved oxygen, impairing physiological functions, and disrupting aquatic food chains. The concentrations observed in this study suggest varying degrees of petroleum pollution across the study area. Continuous monitoring is therefore recommended, especially in locations with consistently elevated TPH concentrations such as Rumuokparali and Mgbuodohia. The findings of this study agree with those of Benson et al. (2018), reported significantly higher TPH concentrations during the dry season in surface waters of the Niger Delta. They attributed this seasonal increase to reduced dilution and continuous petroleum-related activities within the region. Similarly, Nwachukwu et al. (2019) observed that surface waters located close to oil production facilities recorded higher TPH concentrations than less industrialized locations. Their findings support the present observation that Rumuokparali, which is likely exposed to greater anthropogenic activities, recorded the highest TPH concentrations. The present findings are also consistent with Osuji and Onojake (2004), who reported elevated petroleum hydrocarbon contamination in soils and aquatic environments surrounding oil-producing communities in Rivers State. They concluded that frequent oil spills and petroleum-related activities contribute significantly to environmental hydrocarbon contamination.

Furthermore, Adeniji et al. (2017) reported that seasonal fluctuations strongly influence hydrocarbon concentrations in Nigerian aquatic ecosystems, with dry-season concentrations generally exceeding wet-season values due to

reduced dilution effects. This observation closely agrees with the pattern observed in the present study. Internationally, Neff (2002) explained that petroleum hydrocarbons introduced into aquatic systems undergo weathering, volatilization, biodegradation, and sedimentation. However, continuous inputs from anthropogenic sources often exceed natural degradation processes, resulting in persistent contamination, particularly in areas with intensive petroleum activities. Overall, the present findings support previous studies indicating that petroleum hydrocarbon contamination remains a major environmental concern in oil-producing regions, particularly during the dry season when pollutant concentrations tend to increase.

Total Petroleum Hydrocarbon (TPH) in Sediment

The seasonal concentrations of Total Petroleum Hydrocarbon (TPH) in sediment samples from the studied locations revealed marked spatial and seasonal variations (Table 2). The mean TPH concentrations during the wet season ranged from 0.05 ± 0.04 mg/L at Choba to 0.09 ± 0.08 mg/L at Mgbuodohia. In contrast, the dry season recorded substantially higher concentrations, ranging from 0.12 ± 0.01 mg/L at Choba to 0.95 ± 0.05 mg/L at Rumuokparali. This trend indicates that TPH accumulation in sediments is considerably greater during the dry season than during the wet season. The elevated TPH concentrations observed during the dry season may be attributed to reduced rainfall, lower river discharge, and limited dilution of petroleum contaminants. During the wet season, increased rainfall and surface runoff enhance dilution, dispersion, and flushing of hydrocarbons from sediment into surrounding water bodies, thereby reducing TPH concentrations in sediments. Conversely, the dry season promotes the accumulation and persistence of petroleum hydrocarbons due to reduced water movement and increased sedimentation (Abii & Nwosu, 2009; Wang et al., 2013). Among the sampling locations, Rumuokparali recorded the highest dry-season TPH concentration (0.95 ± 0.05 mg/L), followed by Ogbogoro (0.89 ± 0.16 mg/L) and Rumuolumeni (0.83 ± 0.02 mg/L). These elevated values may indicate greater anthropogenic inputs such as petroleum product handling, vehicular emissions, industrial activities, illegal oil bunkering, or runoff from nearby urban settlements. Choba consistently recorded the lowest TPH concentrations in seasons, suggesting comparatively lower hydrocarbon contamination or more effective natural attenuation processes.

The relatively low standard deviations observed for most sampling sites indicate consistency in the measured TPH concentrations, whereas the higher standard deviation at Mgbuodohia during the wet season (0.09 ± 0.08 mg/L) suggests greater variability in hydrocarbon inputs, which may be influenced by episodic runoff events or localized pollution sources. The observed seasonal trend is consistent with previous studies conducted in the Niger Delta and other petroleum-producing regions, where sediment hydrocarbon concentrations are generally higher during the dry season due to reduced dilution and increased contaminant retention (Benson et al., 2018; Osuji et al., 2006). Petroleum hydrocarbons strongly adsorb onto sediment particles because of their hydrophobic nature, making sediments important reservoirs of hydrocarbon pollutants (United Nations Environment Programme (UNEP), 2011). Persistent accumulation of TPH in sediments may adversely affect benthic organisms, alter sediment quality, and pose long-term ecological risks through bioaccumulation within aquatic food webs (ATSDR, 1999). Overall, the findings suggest that seasonal variation significantly influences TPH distribution in sediments, with the dry season exhibiting greater hydrocarbon contamination across all sampled locations. Continuous environmental monitoring and effective pollution control measures are therefore recommended to minimize hydrocarbon inputs and protect aquatic ecosystems in the study area.

Total Petroleum Hydrocarbon (TPH) in blue crab and Periwinkle

The TPH concentration of blue crab (*Callinectes sapidus*) and periwinkle (*Tympanotonus fuscatus*) in the dry season was detected between 0.01 ± 0.00 – 0.02 ± 0.01 mg/Kg. The wet season differed between ND – 0.01 ± 0.00 mg/Kg, (Table 3). The low levels of Petroleum Hydrocarbons (TPH) in the aquatic environment can have a deleterious effect on zooplanktons. The variation in the concentration of TPH in the biota may be due to anthropogenic activities around the river and from atmospheric emissions from numerous automobile exhausts. The level of total Petroleum Hydrocarbons (TPH) in the (*Callinectes sapidus* and *Tympanotonus fuscatus*) is below the the Standard Organization of Nigeria (SON, 2017) Standards of 0.007 mg/l. However, the trace amounts of TPH can bioaccumulate in the body tissue as occupants of the area continue to drink from this river in the long run (Benson et al., 2018). TPH indicated a low concentration range, which was lower than the DPR (2002) recommended standard of 0.6 mg/kg. The seasonal concentration of Total Petroleum Hydrocarbon (TPH) in sea blue crab and periwinkle showed generally low levels across all sampled locations during both the wet and dry seasons. However, slight

seasonal and spatial variations were observed. During the wet season, TPH was not detected (ND) in sea blue crab from Choba and Mgbuodohia, as well as in periwinkle from Mgbuodohia, indicating the absence or concentrations below the analytical detection limit. In contrast, measurable TPH concentrations (0.0 ± 0.00 or 0.00 ± 0.01 mg/l) were recorded in samples from Ogbogoro, Rumuolumeni, and Rumuokparali, suggesting low-level hydrocarbon contamination in these locations. In the dry season, TPH was detected in all samples, with concentrations ranging from 0.01 ± 0.00 – 0.02 ± 0.01 mg/L. The relatively higher concentrations observed during this season may be due to reduced water volume and limited dilution, leading to greater accumulation of hydrocarbons in aquatic organisms (UNEP, 2011). Similar seasonal trends have been reported in aquatic ecosystems of the Niger Delta, where petroleum hydrocarbon concentrations were generally higher during the dry season than the wet season (Nwineewii & Marcus, 2020). The highest concentration (0.02 ± 0.01 mg/L) was observed in periwinkle from Mgbuodohia and in sea blue crab from Rumuolumeni and Rumuokparali. Most other samples recorded 0.01 ± 0.01 mg/L, indicating relatively uniform but low TPH concentration during the dry season. The minor difference between sea blue crab and periwinkle may also reflect differences in their habits and ecological niches. Periwinkles are benthic grazers that remain in close contact with sediments, where hydrocarbons tend to accumulate, while blue crabs are more mobile and may experience varying levels of exposure. This could explain the relatively higher TPH concentration observed in periwinkles at Mgbuodohia. However, the detection of TPH in most samples suggests continuous, albeit low-level, exposure to petroleum-derived contaminants, which is common in the Niger Delta due to oil exploration, transportation, and other anthropogenic activities (Nwineewii & Marcus, 2020).

Conclusion

This study assessed the seasonal variation of hydrocarbon contamination in surface water, sediment, blue crab (*Callinectes sapidus*), and periwinkle (*Tympanotonus fuscatus*) collected from selected locations along the Akpor axis of the New Calabar River. The findings demonstrated that measurable concentrations of TPH were present in all environmental matrices, indicating continuous hydrocarbon inputs into the river ecosystem. The results further showed that hydrocarbon concentration varied between dry and wet seasons, confirming that seasonal changes significantly influence the distribution, transport, and accumulation of petroleum pollutants. Sediments contained relatively higher concentrations than surface water due to their ability to retain contaminants over time, while blue and periwinkle accumulated hydrocarbons from their environment, highlighting their usefulness as bio indicators of aquatic pollution. Although the measured concentrations were generally within WHO (2017) permissible limits, the continuous detection of hydrocarbons suggests persistent anthropogenic activities, including oil exploration, industrial effluent discharge, and urban runoff, which may pose long term ecological risks if left uncontrolled. Continuous pollution may eventually result in bioaccumulation and biomagnification within aquatic biodiversity and human health.

Recommendations

1. Routine monitoring of Total Petroleum Hydrocarbon in surface water, sediment, and aquatic organisms should be conducted during both dry and wet seasons to detect changes in contamination levels and support timely environmental management
2. Regulatory agencies should enforce stricter compliance with environmental regulations governing industrial effluent discharge, oil exploration activities, and waste disposal to minimize hydrocarbon pollution in the New Calabar River.
3. Oil companies and relevant stakeholders should implement effective oil spill prevention measures, maintain pipeline infrastructure, and establish rapid response systems to reduce the release and spread of petroleum hydrocarbons into the aquatic environment
4. Further research should investigate other priority pollutants, such as polycyclic aromatic hydrocarbons (PAHs), heavy metals, and emerging contaminants, and assess the ecological and human risk associated with the long-term consumption of aquatic organisms from the New Calabar River.

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