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ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SHRIMPS AND CRABS AND SOME PHYSICOCHEMICAL PARAMETERS IN SURFACE WATER OF NEW CALABAR RIVER

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Abstract
This research assessed Polycyclic Aromatic Hydrocarbons in shrimps and crabs, also some physicochemical parameters in surface water. Surface water crab and shrimp samples collected from four (4) different locations (Iwofe waterfront, Mgbuodohia waterfront, Abonnema wharf, and Nembe waterfront) were treated according to laboratory standards and examined for some physicochemical parameters and Polycyclic Aromatic Hydrocarbons (PAHs). The sampling was done between March 2021 to May 2021. The parameters examined include pH, conductivity total suspended solids, total dissolved solids, temperature, ºC, Turbidity, salinity, total hardness, Alkalinity, Ammonium, dissolved oxygen, biochemical demand, chemical Oxygen demand, oil and grease sulphate and nitrate, mg/l. It was observed that in all the physicochemical parameters examined, that the which is the dry season march had more prominent values than the wet season may. The polycyclic aromatic hydrocarbons (PAHs) concentration (ppm) examined include the following: Naphthalene, Acenaphthylene, Acenaphthalene, Fluorene, Phenanthrene, Athracene, Fluorantherne, Pyrene, chrysene, Benz (a) anthracene, Benzo(b,k) fluoranthen, Benz(a) pyreneindeno (1,2,3-cd) pyrene, Dibenz (a,h) an thracene, and Benzo (ghi) perylene (ng/g). Analysis in crabs tissue sample: Nembe > Iwofe > Mgbuodohia > Abonnema and crabs exoskeleton sample: Abonnema > Nembe > Iwofe > Mgbuodohia respectively. Results of analysis is shrimps abdomen samples: Mgbuodohia > Nembe > Iwofe > Abonnema while in shrimps head samples: Abonnema > Iwofe > Mgbuodohia > Nembe. The descriptive statistics and one-way Analysis variance (ANOVA) on the variations in physicochemical parameters for the surface water based on locations (Iwofe > Abonnema > Mgbuodohia > Nembe). The difference associated with the site may have originated from the different anthropogenic influences within the sample of rainwater, budging) especially in the case of pH, which has higher values. Analysis of Variance (ANOVA) was used to interpret the results, which showed the significant differences in various locations of the sample. The result of ANOVA revealed, (significant at $p > 0.05$) that, there is no significant difference in the mean levels of physicochemical parameters and polycyclic aromatic hydrocarbons (PAHs) between the two shellfish (shrimps and crabs) species. The result obtained was within the permissible limit(s) or standard set by WHO, USEPA, and NAFDAC. It is therefore recommended for State Government to constantly monitor the water bodies of the New Calabar River, Nigeria.

Keywords: New Calabar River, physiochemical parameters, polycyclic aromatic hydrocarbons (PAHs), Anthropogenic activities shrimps and crab

Introduction
The New Calabar River is linked with other Rivers in some communities of Rivers State and transverse through Rumuolumeni (Iwofe, Mgbuodohia, & Abonnema Wharf). The discharge of effluents materials into the new Calabar River causes intensive environmental hazards and pollution. Scientists and Policymakers are very much concerned regarding the effects of human and aquatic organisms in general to the exposure of chemical compounds in our ecosystem. Water is the most essential liquid required for the sustainability of terrestrial and aquatic ecology. Living organisms include man-required water for personal consumption, industrial, domestic purposes, and also survival on earth. If the water quality is depleted then survival becomes pernicious and termed contaminated when unfits for its intended use by living organisms. The ultimate recipient of all forms of pollutants is natural water bodies (Edori et al. 2020).

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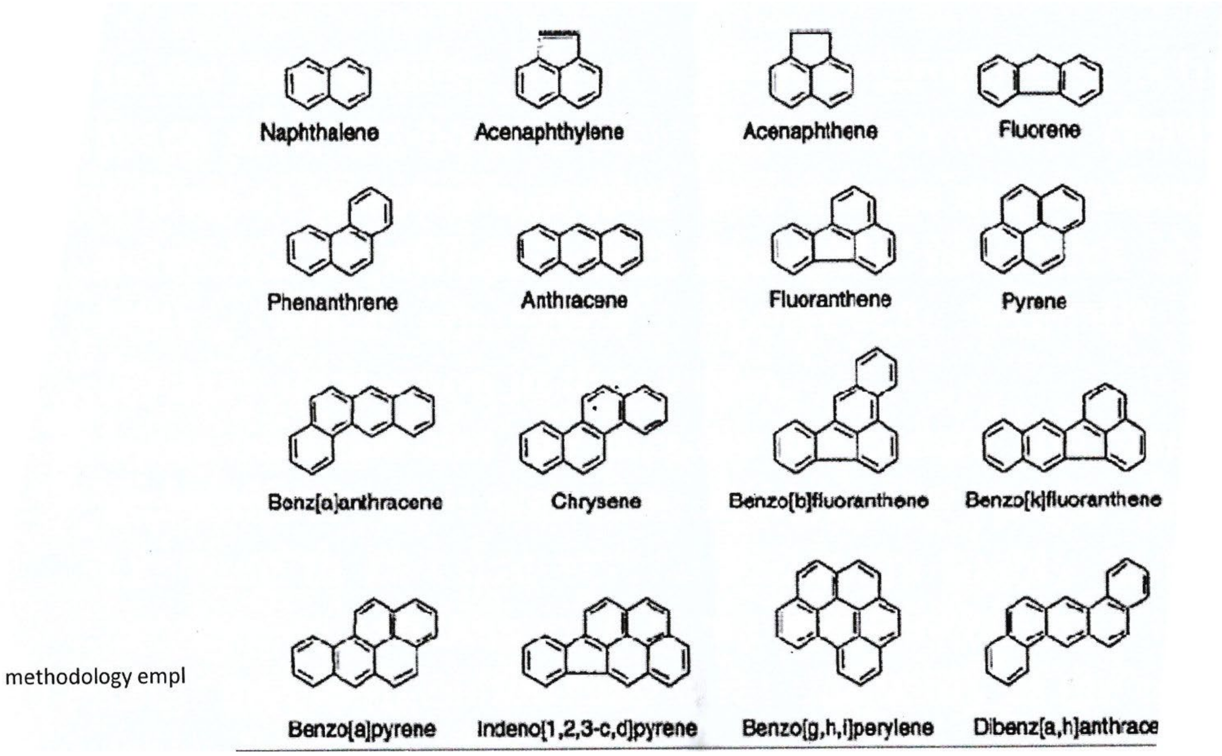
Shrimps (*Penacus notialis)* and crabs (*Portunus Trituberculatus*). These organisms predominantly live in brackish water, fresh water and are generally covered with an exoskeleton. They live in a contaminated aquatic environment with various toxicants such as polycyclic aromatic hydrocarbons (PAHs), heavy metals, plant nutrients, and phenolic compounds (Nwineewii et al., 2019).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic materials (e.g. coal, oil, petrol, and wood). A polycyclic aromatic hydrocarbon (PAH) is a chemical compound containing only carbon and hydrogen which is composed of multiple aromatic rings (Nwineewii et al., 2019).
Physicochemical parameters of the productivity of any water body are dependent on parameters such as temperature, turbidity, conductivity, salinity, pH, BO, BOD, COD, etc. Similarly, the degree of contamination/pollution of the aquatic ecosystem is easily determined by the concentration of these parameters (Kpee, et al., 2020).

Structure of some PAHS



Materials and Methods
The following materials were used; oven (drying oven), volumetric flask/round bottom flasks, sieve, retort stands, heating mantle, funnel (reparatory funnel), Whatman filter paper, Hydrochloric acid HCl, trioxonitrate (iv) and HNO_3, perchloric acid HClO4, soxhlet extractor, laboratory glass wears, test tubes, water bath, beakers, volumetric pipets: 1ml, 5ml, 10ml, desiccator and blender, micro syringes: 10ml, 100ml, 250ml, 500ml, 1000ml, etc, sample containers and bottles, pH meter, thermometer, Do meter and turbidity meter for in-situ measurement, ice-colled box, GPS for geo-referencing sampling locations (Garmin Extrex), Aluminum foil paper.

- **Instrument Condition**
- GC/MS: Agilent Technologies 7890 A equipped with 5975 MSD
- Column: HP-5 Capillary column (30 m, 0.32 mm, 0.25 µm)
- Injection method: Splitless mode
- Injection volume: 1.0µL
- Carrier gas: Helium gas (1.8 mL/min)
- Injection temperature: 280^0C

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- Oven Temp Programme
- MS Mode: Selected Ion Monitoring (SIM)
- MSD Transfer line temp: 280^{0}C

Study Area

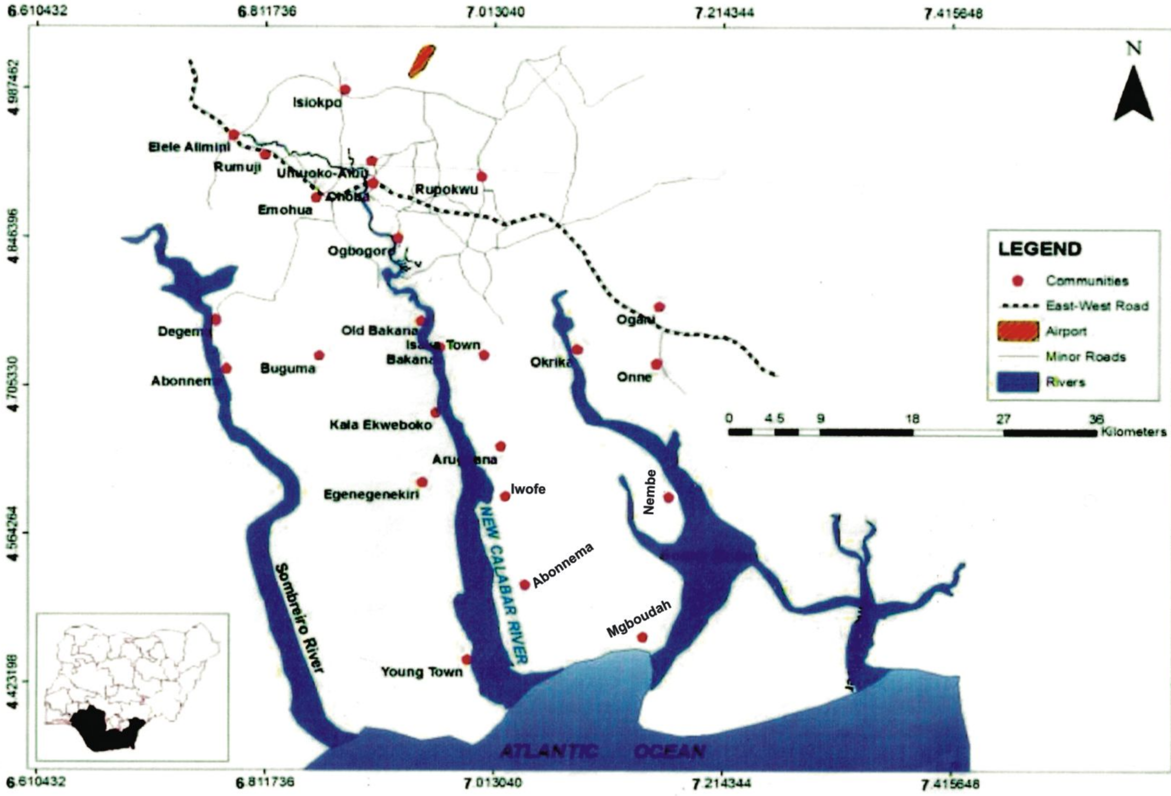

Figure 1: Map of lower Niger Delta showing the New Calabar Rivers drainage system and study area.

Sample Preparation: The separated samples were oven-dried at 105^{o}C then homogenized 50g of the ground sample will be weighed into conical flasks and were digested with the aqua region ($HCl:HNO_3$). Then it was made up to 50ml with distilled water for further analysis.

Statistical Tools: The results from the One-way Analysis variance (ANOVA) on the variations of physicochemical parameters in surface water and Polycyclic Aromatic Hydrocarbons (PAHs) concentration (ppm) in exoskeleton and tissues of shrimps and crab tissue with exoskeleton based on the four different locations.

Sample Analysis: The analysis of shrimps and crab extracts for Polycyclic Aromatic Hydrocarbons (PAHs) was carried out using Gas chromatography.

Sample Collection: Recommended standard methods were used for sample collection. Field sampling and data collection were done following Environmental Guidelines and Standards for the Petroleum Industries in Nigeria (EGASPIN), American Society of Testing of Materials (ASTM), and the American Public Health Association (APHA). A representative of the water sample, crabs, and shrimps from the new Calabar River; Iwofe, Mgboudah, Abonnema Wharf, and Nembe waterfronts were collected using sampling cans and foil paper for surface water, crabs, and shrimps respectively. The sample containers were appropriately labeled with the following information: sample source, date/time of sampling and name of sampler on the field.

At each water sampling location, composite water samples were taken from the surface using 2 litre water samplers. The precaution taken during the sampling of surface water included avoiding contact with the sides and bottom of the sampling points since this could detach slime or sludge accumulated there. Analyses were carried out in the order dictated by the stability of the parameters. All laboratory procedures were adequately standardized and all instruments appropriately calibrated. Samples were collected directly into clean plastic

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containers after rinsing with portions of the water being sampled. The sample containers for the water samples were appropriately labeled.

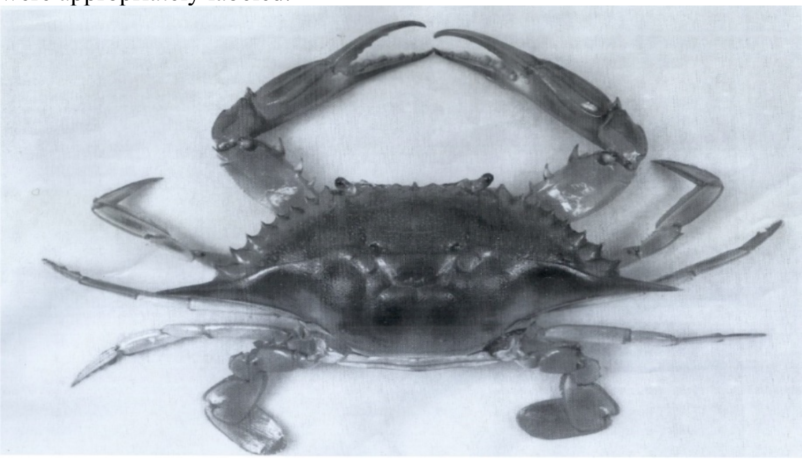

Figure 2: Portumus Crab (Trituberculatus)

Sampling Containers

Samples were collected with glass and plastic bottles subject according to the parameters to be analyzed. The glass and plastic containers were thoroughly washed and sterilized appropriately before use. The following are the containers used for sampling: bvc

- Water samples for physicochemical parameters were collected in 1L plastic bottles
- Water samples for oil and grease analysis were collected in 500ml glass bottles
- Water samples for BOD measurement were collected in dark amber bottles

Samples Preservation

Parameters that vary with time e.g., pH, DO and temperature were determined in-situ, while samples of more stable parameters were preserved (i.e., iced and acidified) to maintain their integrity before analysis in the laboratory. Preservatives were added as required in the specific test methods to avoid changes in the chemical composition of the sample as a result of microbial degradation and inter-chemical reaction.

Figure 3: Shrimp (penaeus notialis)

Quality Assurance/Quality Control (QA/QC)

Internationally accepted methodology such as those of APHA, ASTM, USEPA, DPR, and others prescribed by the FMENV was used. QA/QC includes the regular calibration of field and laboratory instruments and equipment that were used for the EMP. All apparatus, sample containers and glass wares were thoroughly cleaned using standard prescribed methods. Sample blanks and procedural blank were taken and analyzed for each set of samples. Samples were well labeled and transported in the ice-cooled box to maintain their integrity before analysis. All data, both in-situ and ex-situ, were logged inappropriately. Also, the use of chain of custody for quality control.

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Sample Analysis (In-situ Analysis)
Some parameters were then measured in situ, these include; Temperature using a mercury-in-glass, Total, Dissolved, and Suspended Solids using the HACH dissolved solid meter, pH using mettle Toledo, pH meter, Dissolved Oxygen (DO) using YSI DO meter, Conductivity using multi-parameter Meter, and Turbidity using Hanna turbidity meter.

Analytical Methods
Recommended standard analytical methods including those of ASTM and APHA were used for the analysis of samples collected from the field. Specific analytical methods for different physicochemical parameters to be determined in this study are summarized below;

Results
The result of physicochemical parameters in surface water and Polycyclic Aromatic Hydrocarbons (PAHs) is represented in Table 1-6:

Table 1: Results of analysis in the crabs tissue sample

Polycyclic Aromatic Hydrocarbons	Crabs Tissue Abonnema	Crab Tissue Iwofe	Crab Tissue Nembe	Crab Tissue Mgbuodohia
Napthalene (ng/g)	23.89 ± 0.02	41.97±0.10	38.85± 0.50	23.34± 1.30
Acenaphthylene (ng/g)	0.00 ± 0.00	0.00±0.00	0.00 ± 0.00	0.00± 0.00
Acenaphthene (ng/g)	0.00 ± 0.00	0.00±0.00	0.00±0.00	0.00± 0.00
Fluorene (ng/g)	6.31 ± 0.01	22.01±0.02	19.97±0.42	13.52 ±1.00
Phenanthrene (ng/g)	1.33 ± 0.00	4.89±0.01	5.30±0.20	3.55±1.01
Anthracene (ng/g)	1.32 ± 0.00	4.89±0.01	5.30±0.20	3.55±0.02
Fluoranthene (ng/g)	1.02 ±0.00	5.49±0.00	2.30±0.01	1.83± 0.00
Pyrene (ng/g)	0.91+ 0.01	6.04±0.01	22.50±0.50	6.66± 0.03
Benz[a]anthracene (ng/g)	0.24 ± 0.00	1.14±0.00	4.05±0.30	3.01± 0.00
Chrysene (ng/g)	0.17 ± 0.02	0.80±0.01	2.84±0.10	2.12±0.01
Benzo[b,k]fluoranthene (ng/g)	0.00 ± 0.03	0.30±0.03	0.18 ±0.01	0.27± 0.00
Benz[a]pyrene(ng/g)	0.08 ± 0.01	0.30+0.01	0.18±0.00	0.27± 0.00
lndeno[l,2,3-cd]pyrene (ng/g)	0.34 ± 0.00	4.15±0.10	3.01±0.02	7.77± 0.20
Dibenz[a,h]anthraeene (ng/g)	104.82 ± 0.10	994.01± 8.00	1092.77±28.05	778.54±9.00
Benzo[ghi]perylene (ng/g)	0.00 ± 0.00	12.46± 0.07	0.00± 0.00	0.00± 0.00
Mean	**9.37**	**73.23**	**79.82**	**56.30**
SD	**27.11**	**254.97**	**280.45**	**199.90**
PAH(ng/g)	**140.51**	**1098.44**	**1197.23**	**844.43**

***Significant at p>0.05**

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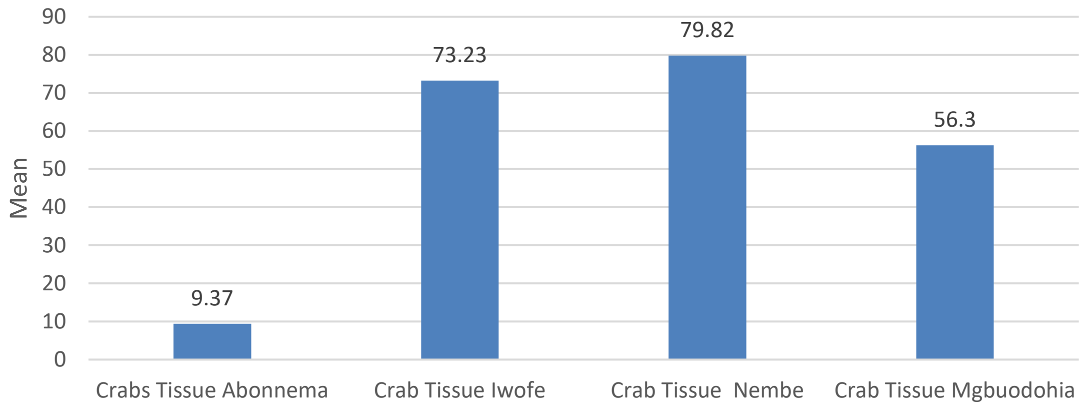

Fig. 4: Composite bar chart on the variations in crab tissue based location

The results obtained in Table 1 and Figure 4 revealed crab tissue in Nembe waterfront has the highest value while crab tissue in Abonnema wharf is the least in the mean value of concentration (ppm) in polycyclic aromatic hydrocarbons (PAHs). The mean concentration (ppm) of PAHs in the four different locations is as follows in the order Nembe (79.82) Iwofe (73.23) > Mgbuodohia (56.30) > Abonnema (9.37). These results revealed that the bioaccumulation at polycyclic aromatic hydrocarbons (PAHs) concentration (ppm) in crab tissue on Nembe waterfront is very high because of the anthropogenic activities in the study area.

Table 2: Results of Analysis in Crabs Exoskeleton Sample

PAHs	**Crab Exoskeleton Abonnema**	**Crab Exoskeleton Iwofe**	**Crab Exoskeleton Nembe**	**Crab Exoskeleton Mgbuodohia**
Napthalene (ng/g)	37.36± 4.06	19.79 ± 6.00	26.51±1.90	3.16±0.60
Acenaphthylene (ng/g)	0.00± 0.00	0.00± 0.00	0.00±0.00	0.00± 0.00
Acenaphthene (ng/g)	0.00± 0.00	0.00±0.00	0.00± 0.00	0.00± 0.00
Fluorene (ng/g)	18.66± 2.00	9.63± 2.00	'16.23±3.00	3.35± 0.20
Phenanthrene (ng/g)	5.16± 1.00	2.98±0.21	4.16 ± 0.50	6.38 ± 2.00
Anthracene (ng/g)	5.16± 1.01	3.01±1.00	4.15± 1.01	7.98 ± 2.01
Fluoranthene (ng/g)	6.22 ± 1.11	2.37 ± 0.00	3.74± 1.00	1.18 ± 0.09
Pyrene (ng/g)	7.26± 1.03	8.83 2.00	2.82±0.01	0.47 ± 0.00
Benz[a]anthracene (ng/g)	4.16± 1.01	2.14± 0.02	1.15 ±0.00	1.91 ± 0.01
Chrysene (ng/g)	2.92± 0.21	1.50± 0.90	0.81± 0.01	1.34±4.62
Benzo[b,k]fluoranthene (ng/g)	0.48 ± 0.00	0.18 ± 0.10	0.50± 0.02	0.10 ± 0.03
Benz[a]pyrene(ng/g)	0.48± 0.00	0.18 ± 0.01	0.50±0.02	0.10 ± 003
lndeno[l,2,3-cd]pyrene (ng/g)	16.89 ± 2.03	3.92 ± 0.99	2.58±1.00	0.49± 0.01
Dibenz[a,h]anthraeene (ng/g)	865.14±22.99	401.25±102.73	723.35±10.75	17.10±4.62
Benzo[ghi]perylene (ng/g)	0.00± 0.00	0.00 ± 0.00	0.00±0.00	0.05±4.62
Mean	**64.66**	**30.39**	**52.43**	**2.91**
SD	**221.67**	**102.73**	**185.75**	**4.62**
PAH(ng/g)	**969.86**	**455.77**	**786.5**	**43.61**

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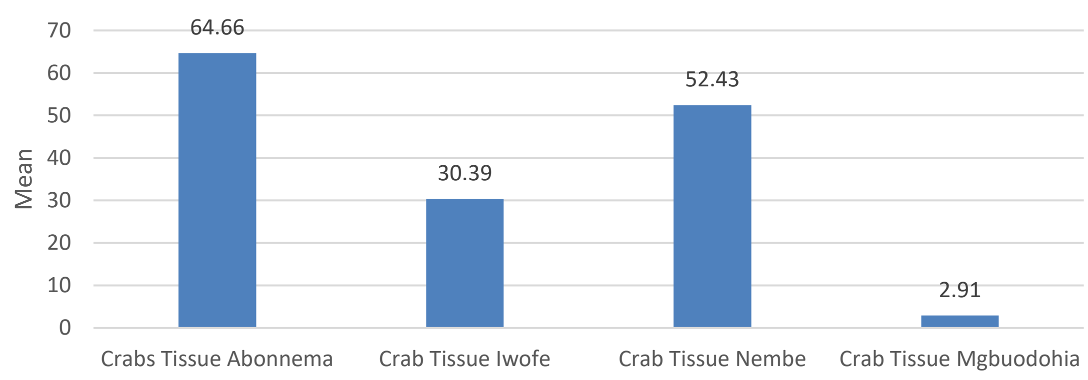

Fig. 5: Composite bar chart on the variations in PAHs in crab exoskeleton based on location

In the crab exoskeleton, sample results showed that Abonnema wharf recorded the highest polycyclic aromatic hydrocarbons (PAHs) concentration and the lowest concentration was Mgbuodohia. The order was Abonnema wharf (64.66) > Nembe waterfront (52.43) > Iwofe waterfront (30.39) > Mgbuodohia waterfront (2.91). Table 2 and Figure 5 revealed high value in Abonnema wharf, this could be attributed to the fact that human activities are more such as bunkering, shipping of crude oil, importation, and exploitation of other materials happening in these locations.

Table 3: Results of Analysis in Shrimps Abdomen Sample

PAHs	Shrimps Abdomen Abonnema	Shrimps Abdomen Iwofe	Shrimps Abdomen Nembe	Shrimps Abdomen Mgbuodohia
Napthalene (ng/g)	6.48± 2.09	21.48±7.06	18.44±5.47	9.75±3.29
Acenaphthylene (ng/g)	0.00± 0.00	0.00±0.00	0.00±0.00	0.00±0.00
Acenaphthene (ng/g)	0.00± 0.00	0.00±0.00	0.00±0.00	0.00±0.00
Fluorene (ng/g)	3.42± 1.00	3.58±1.07	8.31±4.00	12.09±2.20
Phenanthrene (ng/g)	20.56±5.02	4.44±0.76	2.31±0.47	3.4.8±0.99
Anthracene (ng/g)	18.38±4.02	432±37.76	231±115.40	3.48±0.03
Fluoranthene (ng/g)	1.46±20.50	3.08±0.30	1.43±0.07	3.63±0.01
Pyrene (ng/g)	1.71± 0.12	1.56±0.07	1.51±0.09	1.90±0.00
Benz[a]anthracene (ng/g)	0.99±0.01	0.19+0.08	0.12±0.00	0.42± 0.04
Chrysene (ng/g)	0.70±0.05	0.13±0.04	0.42±0.04	0.29± 0.10
Benzo[b,k]fluoranthene (ng/g)	0.11± 0.10	0.04±0.00	0.07±0.00	0.37 ± 0.02
Benz[a]pyrene(ng/g)	0.11± 0.10	0.04±0.00	0.07±0.00	0.37± 0.02
lndeno[l,2,3-cd]pyrene (ng/g)	0.51±0.02	0.57±0.20	1.14±0.02	0.00± 0.00
Dibenz[a,h]anthraene (ng/g)	107.39± 27.32	147.55±37.76	526.90±105.47	832.38± 24.02
Benzo[ghi]perylene (ng/g)	0.09± 0.00	0.11±0.10	0.00± 0.00	0.00± 0.00
Mean	**10.79**	**12.4**	**37.54**	**57.88**
SD	**27.52**	**37.76**	**135.47**	**214.29**
PAH(ng/g)	**161.91**	**187.11**	**563.04**	**868.15**

***Significant at p>0.05**

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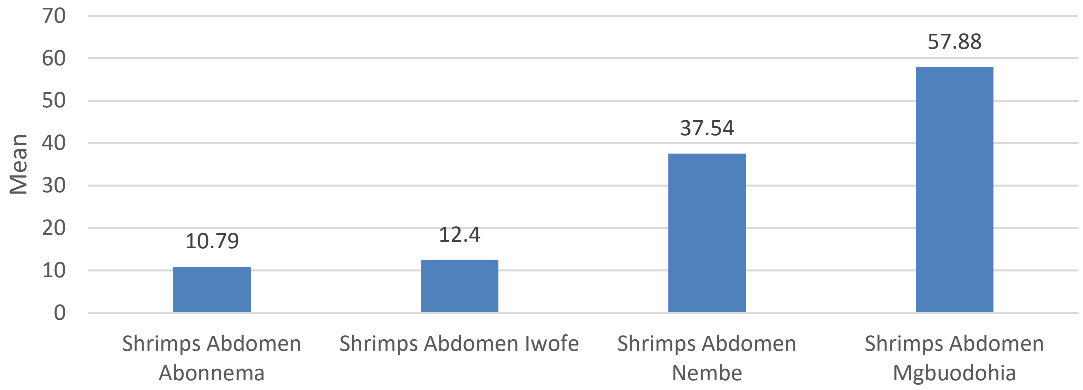

Fig. 6: Composite bar chart on the variation in the PAHs concentrations in the abdomen of shrimps based on location

Table 3 and Figure 6 results in shrimps abdomen revealed that Mgbuodohia location has the highest mean concentration (ppm) of polycycle aromatic hydrocarbons (PAHs) followed by Nembe waterfront, Iwofe waterfront, and Abonnema wharf (57.88 > 37.54 > 12.47 > 10.79) respectively. The New Calabar River has remained trading and fishing routes up to date, which provides an economic lifeline for so many people. The high level of industrial activities and company like Nigerian Agip Oil company (NAOC) in Mgbuodohia location pose great environmental challenges to the community and the region at large.

Table 4: Results of Analysis in Shrimps Head Sample

PAHs	Shrimps Head Abonnema	Shrimps Head Iwofe	Shrimps Head Nembe	Shrimps Head Mgbuodohia
Napthalene (ng/g)	18.70±4.00	8.28± 2.01	23.82±7.20	4.06±0.20
Acenaphthylene (ng/g)	0.00±0.00	0.00±0.00	0.00±0.00	0.00± 0.00
Acenaphthene (ng/g)	0.00±0.00	0.00±0.00	0.00±0.00	0.00± 0.00
Fluorene (ng/g)	15.09±4.01	7.23± 3.00	15.94±0.22	5.35±0.09
Phenanthrene (ng/g)	5.91± 1.07	2.82±0.02	11.13±2.02	1.95± 0.01
Anthracene (ng/g)	5.91±1.07	2.82± 0.02	10.98±2.00	1.94± 0.01
Fluoranthene (ng/g)	4.72± 0.99	4.42±1.02	7.43± 1.00	3.33±1.00
Pyrene (ng/g)	39.59± 0.84	1.07± 0.00	3.20± 0.30	0.81 ± 0.00
Benz[a]anthracene (ng/g)	13.22±2.80	0.00±0.00	11.79±1.22	0.15 ± 0.00
Chrysene (ng/g)	9.27±2.84	0.00±0.00	8.27± 2.00	0.10± 0.00
Benzo[b,k]fluoranthene (ng/g)	0.11±0.08	0.19±0.01	0.32± 0.00	0.25± 0.00
Benz[a]pyrene(ng/g)	0.11±0.08	0.19±0.01	0.32±0.00	0.25± 0.01
lndeno[l,2,3-cd]pyrene (ng/g)	1.40±0.84	1.99± 0.10	3.27±0.90	1.65 ±0.09
Dibenz[a,h]anthraeene (ng/g)	862.48±20.84	751.10±19.42	0.00±0.00	584.24±15.49
Benzo[ghi]perylene (ng/g)	0.00± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00±0.00
Mean	**65.10**	**52.01**	**6.43**	**40.27**
SD	**220.84**	**193.42**	**7.22**	**150.49**
PAH(ng/g)	**976.54**	**780.11**	**96.47**	**604.08**

***Significant at p>.05**

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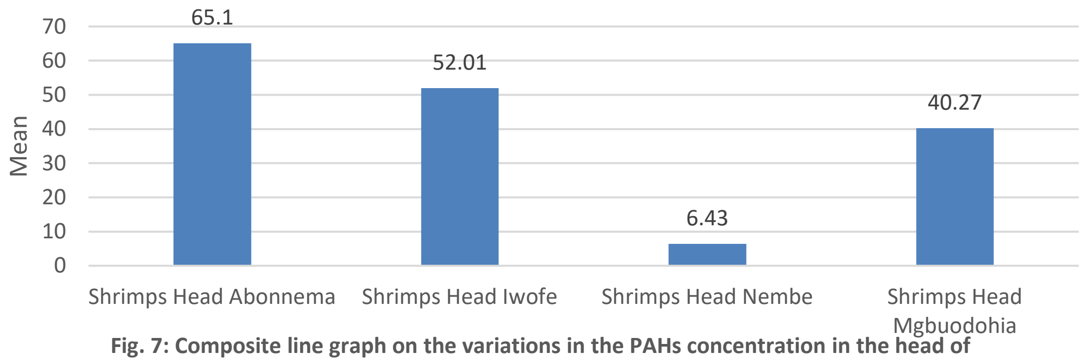

Fig. 7: Composite line graph on the variations in the PAHs concentration in the head of shrimps based on location

Table 4 and Figure 7 are the results of the analysis in shrimps head in the four different locations that revealed the least value at Nembe waterfront (6.43) in concentration (ppm) at polycyclic aromatic hydrocarbons (PAHs) and the highest mean value was Abonnema wharf (65.10). This study showed the illegal industrial activities such as those from illegal oil bunkers ongoing on the Abonnemawharf waterfront.

table 5: Physicochemical analysis result of surface water: May

S/No	Parameters	Methods	DPR Limit	FMENV limit	Physicochemical Analysis of New Calabar River			
					Iwofe waterfront	Mgbuodohia water front	Abonnema wharf waterfront	Nembe waterfront
1	pH	Meter	6.5 – 8.5	6-9	6.32±2.10	6.93±3.00	6.78±38.58	6.38
2	Temperature, oC	Meter	NS	<40	30.20±8.07	29.38±3.59	28.21±38.58	30.80
3	Turbidity, NTU	Meter	0.2		28.14±1.09	24.60±3.08	17.40±38.58	9.27
4	Conductivity, µs/cm	Meter	NS		420.00±107.90	128.00±33.50	14.00±38.58	11.00
5	TSS, mg/l	ASTM D5907	30	30	44.54±10.00	53.646±23.50	43.970±38.58	37.600
6	TDS, mg/l	Meter	<600		210.00±107.91	64.00±30.58	74.00±38.58	57.00
7	Salinity (as Cl), mg/l	ASTM D512	NS		9.50±107.91	6.49±3.05	8.99±38.58	5.99
8	Total Hardness, mg/l	APHA 2340	500		44.00±7.91	22.00±3.58	16.00±38.58	10.00
9	Alkalinity , mg/l	APHA 2320			14.00±2.05	50.00±33.50	60.00±38.58	30.00
10	Ammonium, mg/l	APHA 4500			0.48±0.01	0.33±0.00	0.148±38.58	0.284
11	DO, mg/l	Meter			3.89±0.91	3.65±0.70	3.81±38.58	3.88
16	BOD, mg/l	APHA 5210	10		2.80±0.05	3.10±1.01	2.98±38.58	3.02
17	COD, mg/l	APHA 5220	40		9.00±0.00	12.30±3.58	14.00±38.58	17.10
18	Oil and Grease, mg/l	ASTM D7678	0.6		<0.01±0.00	<0.01±0.00	<0.01±38.58	<0.01
19	Sulphate, mg/l	APHA 4500	0.1		2.50±0.91	7.23±1.18	2.47±38.58	1.011
20	Nitrate, mg/l	APHA 4500	50		0.35±0.09	1.10±0.00	0.27±38.58	0.833
21	Phosphate, mg/l	APHA 4500			1.38±)0.01	4.81±1.08	1.57±38.58	1.440
			Mean		**51.67**	**26.09**	**26.78**	**20.54**
			SD		**107.91**	**33.58**	**38.58**	**29.30**

***Significant at p<.05**

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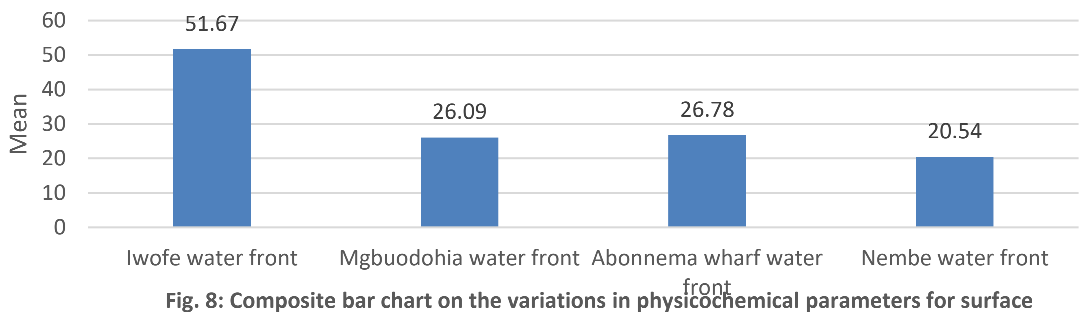

Fig. 8: Composite bar chart on the variations in physicochemical parameters for surface water based on location

The results in the wet season showed that Iwofe waterfront has the highest mean value of physicochemical parameters in surface water analysis and the lowest was Nembe waterfront. All the mean values of the physicochemical parameters are within the permissible limit. The p-value (p>0.05) showed in the results has no statistically significant difference.

Table 6: Physicochemical analysis result of surface water

S/no	Parameters	Methods	DPR limit	FME NV limit	Iwofe waterfront	Mgboudohia waterfront	Abonnema wharf waterfront	Nembe waterfront
1	pH	Meter	6.5 – 8.5	6-9	7.21± 1.02	7.03±1.60	7.92±22.16	7.38±16.84
2	Temperature, oC	Meter	NS	<40	28.31±8.10	27.02±5.40	29.44±22.16	28.65±16.84
3	Turbidity, NTU	Meter	0.2		30.21± 9.99	18.71±5.00	29.20±22.16	15.28±16.84
4	Conductivity, µs/cm	Meter	NS		640.00± 42.02	214.00±55.40	42.00±22.16	32.00±16.84
5	TSS, mg/l	ASTM D5907	30	30	82.30± 22.01	71.64±5.30	62.52±22.16	53.47±16.84
6	TDS, mg/l	Meter	<600		320.00± 35.01	107.00±50.40	21.00±22.16	16.00±16.84
7	Salinity (as Cl), mg/l	ASTM D512	NS		58.11±12.00	39.67±5.99	35.77±22.16	28.90±16.84
8	Total Hardness, mg/l	APHA 2340	500		67.00±15.01	42.00±5.63	31.00±22.16	28.00±16.84
9	Alkalinity , mg/l	APHA 2320			19.00± 7.00	64.00±5.90	71.00±22.16	48.00±16.84
10	Ammonium, mg/l	APHA 4500			0.80 ±0.01	0.70±0.20	0.53±22.16	0.37±16.84
11	DO, mg/l	Meter			4.30±1.00	4.02±1.04	4.32±22.16	4.17±16.84
12	BOD, mg/l	APHA 5210	10		4.80± 1.00	6.10±0.40	2.98±22.16	4.02±16.84
13	COD, mg/l	APHA 5220	40		16.00± 0.29	14.30±4.20	8.00±22.16	12.10±16.84
14	Oil and Grease, mg/l	ASTM D7678	0.6		<0.01 ±0.00	<0.01±0.00	<0.01±22.16	<0.01±16.84
15	Sulphate, mg/l	APHA 4500	0.1		3.21± 0.01	12.51±5.00	8.02±22.16	3.17±16.84
16	Nitrate, mg/l	APHA 4500	50		0.74± 0.10	1.44±0..40	1.23±22.16	1.94±16.84
17	Phosphate, mg/l	APHA 4500			1.90± 0.02	6.81±55.40	2.21±22.16	2.72±16.84
			Mean		**80.24**	**39.80**	**22.32**	**17.88**
			SD		**168.53**	**55.40**	**22.16**	**16.84**

***Significant at p=.05**

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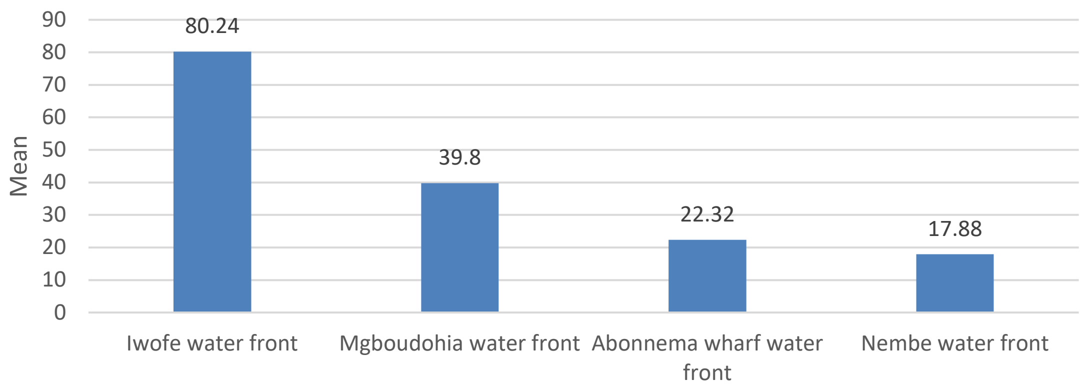

Fig. 9: Composite bar chart on the variations in physicochemical parameters for surface water based on location

In Table 6 and Figure 9 at physicochemical parameters analysis result at surface water in the dry season, the highest mean value is Iwofe location followed by Mgbuodohia while the least is Nembe waterfront location. The results from the descriptive statistics and one-way ANOVA on the variations in physicochemical parameters for surface and polycyclic aromatic hydrocarbons (PAHs) in shrimp tissues and exoskeleton with the crab tissues and exoskeleton varied based on locations. The results obtained from this study are related to most of the reviewed literature (Marcus & Ikoedem, 2021; Kpee et al., 2020; Marcus & Ekpete, 2014).

Conclusion

The concentrations of physicochemical parameters that were investigated in the four sampling locations fell within the Department of Petroleum Resources (DPR) and World Health Organization (WHO)regulatory requirements with exception of Dissolved Oxygen, turbidity, total suspended solids, total hardness, and sulphate. This assessment is in line with Kpee et al. (2020) on physicochemical parameters. There are variations in the physicochemical parameters of water quality studied due to ecological variations of the sampling stations, transport activities /waste generated by the operations of vessels at the ports, and anthropogenic activities in the Niger Delta region which have contributed to the concentration of pollutants in the water bodies. The results correspond to the review of Marcus and Ekpete (2014) research on the impact of the discharged process of wastewater. The concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in the abdomen, head, tissues, and exoskeletons of shrimps and crabs across four sample locations showed that they were at trace level. However, continuous bioaccumulation of this pollutant could make them unfit for consumption thereby endangering human health.

Recommendations

1. New Calabar River needs to be protected against contamination and pollution to minimize the potentially associated shrimps, crab, surface water, and aquatic organisms in the area.
2. Exposure of aquatic organisms to a contaminated environment is to monitor the effects of polycyclic aromatic hydrocarbons (PAHs) on the early stages of life such as the larvae of fishes, crabs, shrimps, and egg that is in the reproductive stages in the New Calabar Rivers of Niger Delta Area in Nigeria, African.
3. The Federal Government via the Federal Ministry of Environment in collaboration with the National Agency for Food and Drug Administration and Control (NAFDAC) should establish guidelines.
4. Regulatory bodies should monitor industries to ensure that they treat their wastes before disposal and regular check should be carried out to find out the state of the water bodies from time to time in other to preserve the lives of aquatic organisms including crabs and shrimps.
5. Government should also monitor the content of discharged effluent and activities of oil and gas companies operating and other phylogenic activities within the study area to cub further increase in concentrations of the PAHs components.

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