

Evaluation of Heavy Metals and Total Hydrocarbon Contents in *Crassostrea Spp* (Oysters) from Qua Iboe River, Ibeno LGA

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Abstract: This study evaluates the level of heavy metals and total hydrocarbon content in *Crassostrea spp.* (oysters) at Qua Iboe River, Ibeno LGA. Heavy metals analysis was carried out using the Atomic absorption spectrophotometer (AAS) while the total hydrocarbon content (THC) was determined with Gas chromatography fitted with flame ionization detector (GC-FID). The oysters were selected randomly at three sample study areas analyzed for heavy metal and THC. The results for lead, copper, cadmium and nickel analysis showed that the mean metal concentration at site A were as follows: Pb (1.014 ± 0.011 mg/kg), Cu (0.067 ± 0.089 mg/kg), Ni (0.029 ± 0.006 mg/kg), Cd (0.001 ± 0.001 mg/kg); site B - Pb (1.033 ± 0.003 mg/kg), Ni (1.027 ± 0.010 mg/kg), Cu (0.045 ± 0.010 mg/kg), Cd (0.003 ± 0.002 mg/kg) and site C (control) - Ni (1.025 ± 0.002 mg/kg), Pb (0.01 ± 0.001 mg/kg), Cu (0.001 ± 0.001 mg/kg), Cd was below detection limit (BDL). The total hydrocarbon content at site A was (141244.0 ± 6801.3 mg/kg), site B (172130.4 ± 25703.1 mg/kg) and site C (1894.7 ± 94.3 mg/kg). Health risk was estimated to assess the total hazard quotient (THQ) of heavy metals at the study sites. The estimated daily intake of heavy metals at the study sites were: site A Pb (2.589 mg/kg), Cd (0.003 mg/kg), Cu (0.171 mg/kg) and Ni (0.072 mg/kg). THQ at site A of Pb was 2.7795, Cd (0.0096), Cu (0.0174) and Ni (0.0005), site B Pb (2.8316) was the highest followed by Ni (0.4927), Cu (0.01167) and Cd (0.0288) and site C (control) Ni (0.4917) was the highest followed by Pb (0.0027) and Cu (0.0003). The THQ results from site C were below 1 and as such the oysters were safe for consumption. The total hazard quotient for sites A and B, for Cu Cd and Ni were less than 1 and Pb greater than 1, implying that the oysters from sites A and B were not safe and will pose an appreciable hazard to humans for the metal pollutants. Statistically, there was no significant difference because the $P_{0.05}$ -value was greater than alpha ($p > 0.05$).

Keywords: Heavy Metal, Total Hydrocarbon, *Crassostrea Spp.* (Oysters), Total Hazard Quotient

1. Introduction

Over the years, a large amount of toxic pollutants has been directly or indirectly discharged into the marine ecosystem. Total hydrocarbon content and heavy metals account for the majority of the pollutants in the marine ecosystem [17, 19] Hydrocarbon pollution of the environment is a very serious problem of the Niger Delta ecosystems in Southern Nigeria due to the heavy oil exploration activities, resulting in poor oil waste disposals and accidental spills. This concern is worsened by the fact that total hydrocarbons contents are highly lethal to life both plants and animals respectively.

Hydrocarbons can cause different health effects in aquatic animals; damage to organs and systems such as kidney, liver, circulatory system etc. could result in a wide array of diseases, disorders and diseased conditions [1]. Humans are especially susceptible to the harmful effects of hydrocarbons. Symptoms of hydrocarbon toxicity may be visible upon exposure or accumulated over a period of time.

By definition, heavy metals (HMs) are loosely defined as members of a subset of elements that have density above 5.0 g cm^{-3} , exhibiting metallic properties and are chemically toxic to plants and animals [8]. Examples include Mercury (Hg), lead (Pb), Iron (Fe), Cadmium (Cd), Copper (Cu), Arsenic

(As), Thallium (Tl), Manganese (Mn), Nickel (Ni), Vanadium (V) and Selenium (Se). The most important metals with regards to potential toxic effects are As, Cd, Cr, Hg, Pb and Zn; and Metals which in small quantities are essential for healthy growth but when in excess become hazardous include Co, Cu, Mn, Ni and Se respectively.

The non-nutrient heavy metal has been of great concern to the public health since they are toxic at very low concentration on ingestion, with no identifiable deficiency symptoms [10, 26].

Apart from sediments, the aquatic animals have been used to assess the impact of pollution in the surrounding environment Ubong *et al.* [28] Oyster is bivalve molluscs with rough irregular shells that live in marine or brackish water. Edible oyster mainly belongs to genera *Ostrea*, *Crassostrea*, and *Saccostrea*. *Crassostrea* species are euryhaline and occurs at intertidal and subtidal level in creeks, bays, estuaries and invades up to 100 feet, coastal shallows and inshore zone. They attach themselves to a hard substratum such as rocks, stones, dead shells, corals, concrete cements, shipwrecks and covers extensive areas in coastal and estuarine regions. Then intertidal/sub tidal biogenic structures formed due to large aggregation of oysters and building of a habitat with significant surface complexity is known as oyster beds, oyster bottoms, oyster bars, oyster banks, or oyster reefs Bahr and Lanier [6]. This study therefore, utilizes *Crassostrea* spp. as a bio-indicator for assessing the level of pollution of Qua Iboe River in Ibeno Local Government of Akwa Ibom State.

2. Location of Study Area

The area under study is the Qua Iboe River, in Ibeno Local Government Area, Akwa Ibom State located in the Niger Delta region of Nigeria. The Qua Iboe River flows southward into the Atlantic Ocean, where it forms an estuary at Mkpanak Village. The river rises near Umuahia in Abia state, Nigeria, and flows in south eastern direction through Akwa Ibom State to the Atlantic Ocean. The river feeds a zone of

mangrove swamps linked by creeks and lagoons that is separated from the sea by a low and narrow ridge of sand. It lies between latitude 4°30"N and 5°30"N and long 7°30"E and 8°15"E. The control site for the study was Etinan Local Government Area, because it was free from oil exploration and other kinds of marine commercial activities.

2.1. Site Selection

The samples were collected at three different stations; two from the site close to the oil polluted Area and the other one from the control station.



Figure 1. Internal view of *Crassostrea* spp.



Figure 2. External view of *Crassostrea* spp.

2.2. Description of Sampling Site



Figure 3. The map showing the study area.

The samples were collected from three different sites, two were from Nditia community, Ibeno local Government of Akwa Ibom State having a latitude between $04^{\circ}34'56.74''\text{N}$ and $04^{\circ}34'02.6''\text{N}$ and longitude between $07^{\circ}54'50.96''\text{E}$ and $07^{\circ}58'25.9''\text{E}$ respectively. The third site was the control located in Ikot Ibok community, Etinan Local Government Area having latitude of $4^{\circ}47'0.50''\text{N}$ and a longitude of $7^{\circ}52'55.80''\text{E}$.

3. Methods of Research

3.1. Sample Collection and Preservation

The oysters samples were obtained randomly at the three different sampling stations in the study site, placed in a cooler and taken to the laboratory for analysis of Lead (Pb), Cadmium (Cd), Nickel (Ni), Copper (Cu) and Total Hydrocarbon contents (THC). All reagents used for analysis were of analytical grade.

3.2. Determination of Total Hydrocarbon Contents (THC) in Oysters

Total hydrocarbon content (THC) was determined using Gas chromatography fitted with flame ionization detector (GC-FID). The extraction method outlined by Schwab, *et al* [21] was applied to the samples as follows; the samples were cut into pieces and then crushed using mortar and pestle. 10g of each of the crushed samples were weighed into a 100ml beaker and 60 ml of THC extraction mixture (250 ml of acetone and 250 ml of dichloromethane) was then added. The beaker with its contents was placed on a magnetic stirrer (with heater) and shaken for about 25 mins at 70°C . The extract was later decanted into a flask and 30 ml of fresh extraction solvent was added; followed by constant shaking on the magnetic stirrer. 5 g of anhydrous sodium sulphate was used to remove water from the extract, which was concentrated to 3ml with rotary evaporator maintained at 20°C . 1.5ml of the concentrated extract was loaded on silica gel column and eluted with 30ml HPLC-hexane into a well labeled 100 ml beaker to get the aliphatic hydrocarbon components in the sample. Then 30 ml of chloromethane was used to elute the aromatic hydrocarbon contents into another labeled 100 ml beaker. 2g of anhydrous sodium sulphate was added to remove any traces of water left in the extract. The extracts were re-concentrated using rotary evaporator to about 2 ml. 1ml of extract was taken and transferred into a well labeled chromatography vial for gas chromatography analysis. The samples were stored at temperature of 4°C until GC analysis.

3.3. Determination of Heavy Metals

The Oysters samples were digested after drying at a temperature of 105°C for 24 hours according to [4] methods. The levels of Pb, Cd, Cu and Ni was determined using bulk scientific model 210VGP (variable giant pulse) atomic absorption spectrophotometer with different hollow cathode

lamp at different wavelength. The dried samples were grinded using mortar and pestle and 1g of each sample was weighed into digestion flask. 10ml of ratio 10:1 mixture of Nitric acid (HNO_3) and Perchloric acid (HClO_4) acid were added to the sample in each digestion flask, swirled clamped and allowed for some minutes for any reaction to subside. The digestion flask was mounted on a heating mantle and heating began gradually until appearance of whitish dense fumes and a clear solution was obtained. The digestion flask was removed and allowed to cool. 50 ml of deionized water was added to the digest filtered and made up to mark of 100 ml standard volumetric flask with deionized water. Each of the standard volumetric flask of the digest were corked, labeled and stored in the refrigerator for AAS analysis.

3.4. Moisture Content Determination

Water content in Oysters samples was determined by drying a known weight (1g) in an oven to a constant weight at a suitable temperature of 105°C . The loss in weight was due to moisture loss and calculated in terms of percentage weight of the samples with the formula;

$$\% \text{ Moisture} = \frac{W_1 - W_2}{W_1} \times 100$$

Where W_2 = weight of sample after drying

W_1 = weight of sample before drying

3.5. Ash Content Determination [5]

The ash content of the samples was determined by burning the dry samples in an enclosed muffle furnace at temperature of 500°C for 4 hours until the samples turned to ash and the value expressed in terms of dry weight of the samples. The organic matter was obtained by subtracting the amount of the ash from the dry samples.

3.6. Health Risk Assessment

Uptake of heavy metals by consuming *Crassostrea spp.* (oysters) or the estimated daily intake (EDI), can be calculated using the following formula:

$$\text{EDI} = \frac{C \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}$$

Where C (mg/kg) is the concentration of heavy metals in the oysters obtained from the analysis, IR (ingestion rate), is the rate of consumption of oysters a day (160g/day/person) [2].

EF is the exposure frequency (365days/year) ED (54 years) is the duration of the exposure and is usually calculated according to the study objective for a period of one year or 365 days). AT is the average exposure to non-carcinogens for 365 days/year and multiplied by ED. BW is the average weight which is 62.65kg.

Hazard quotient (HQ) is the ratio used for the characterization of risk and also to estimate whether a particular risk has a significant impact. HQ is calculated

using the following equation:

$$HQ = \frac{EDI}{RfD}$$

The THQ was calculated using the formula:

$$THQ = \frac{EF \times ED \times FIR \times C}{RfD \times WAB \times TA} \times 10^{-3}$$

EF is the exposure frequency (350days/year). ED is the exposure duration (54years). FIR is the food ingestion rate (60g/person/day). C is the metal concentration. RFD is the oral reference dose (mg/kg). Average body weight (WAB) is 60kg. TA is the average exposure time for non-carcinogenic (ED×365days/year). Oral reference dose (RFD) for the metals are: [Pb; 0.0035 mg/kg/day. Cd; 0.001 mg/kg/day. Ni; 0.020 mg/kg/day and Cu; 0.037 mg/kg/day [23].

If the THQ is greater than 1, the exposure is likely to cause

obvious adverse effects.

4. Result and Discussion

4.1. Result

The result in Table 1 and Figures 4 - 6 shows the descriptive statistical analysis of heavy metals in oysters from the three sampling sites, Table 2 and Figure 7 illustrate the descriptive statistical analysis of total hydrocarbon content in oysters while Table 3 presents the proximate analysis for heavy metals and total hydrocarbon content in oysters from the area of study. Table 4 shows the summary of Estimated Dietary Intake and Total Hazard Quotients in Oysters.

Table 1. Descriptive Statistical analysis of heavy metals in *Crassostrea* spp. (oysters).

SITES	METAL	RANGE (mg/kg)	MEAN (mg/kg)	STANDARD DEVIATION (mg/kg)	*FAO LIMITS
A	Pb	1.001-1.021	1.014	0.011	1.0
	Cd	0.001-0.002	0.001	0.001	1.0
	Cu	0.014-0.018	0.067	0.089	30.0
	Ni	0.022-0.033	0.029	0.006	NA
B	Pb	1.031-1.037	1.033	0.003	1.0
	Cd	0.001-0.005	0.003	0.002	1.0
	Cu	0.033-0.051	0.045	0.010	30.0
	Ni	1.023-1.029	1.027	0.003	NA
C (control)	Pb	0.001-0.002	0.001	0.001	1.0
	Cd	BDL	BDL	BDL	1.0
	Cu	0.001-0.002	0.001	0.001	30.0
	Ni	1.023-1.027	1.025	0.002	NA

FAO LIMITS, (2003)

Table 2. Descriptive statistical analysis of total hydrocarbon contents in *Crassostrea* spp. (Oysters).

SITES	RANGE (mg/kg)	MEAN CONCENTRATION (mg/kg)	STANDARD DEVIATION (mg/kg)
SITE A	134,512.11-148,112.67	141,244.0	6801.3
SITE B	144,976.08-196,082.10	172130.4	25703.1
SITE C (control)	1810.09-1996.00	1894.7	94.1

Table 3. Proximate analysis for the level of heavy metals and total hydrocarbon content in *Crassostrea* spp. (oysters).

SAMPLE	pH	TEMPERATURE (°C)	MOISTURE CONTENT	ASH CONTENT
Oysters	5.71±0.03	27.20±0.01	8.09±0.03	0.04±0.03

Table 4. Summary of Estimated Dietary Intake (EDI) and Total Hazard Quotients (THQ) in *Crassostrea* spp. (Oysters).

SITES	METAL	EDI (mg/kg)	THQ
SITE A	Pb	2.606	2.7795
	Cd	0.003	0.0096
	Cu	0.172	0.0174
	Ni	0.075	0.0005
SITE B	Pb	2.655	2.8316
	Cd	0.008	0.0288
	Cu	0.116	0.0117
	Ni	2.640	0.4927
SITE C (control)	Pb	0.003	0.0027
	Cd	BDL	BDL
	Cu	0.003	0.0003
	Ni	2.635	0.4917

4.2. Concentration of Heavy Metals

4.2.1. Site A

At site A Pb range from 1.001-1.021 mg/kg with mean concentration 1.014± 0.011 mg/kg which were slightly above FAO [11] permissible limit of 1.0 mg/kg (Table 1 and Figure 4.), Cd varies from 0.001-0.002mg/kg with mean levels of 0.001±0.001mg/kg which was below the FAO [11] limit of 1.0 mg/kg. The concentration of Cu was between 0.014-0.018 mg/kg with mean of 0.067±0.089 mg/kg, this was lower than the FAO [11] permissible limit of 30.0 mg/kg, Ni range from 0.022-0.033 mg/kg with mean concentration of 0.029±0.006 mg/kg.

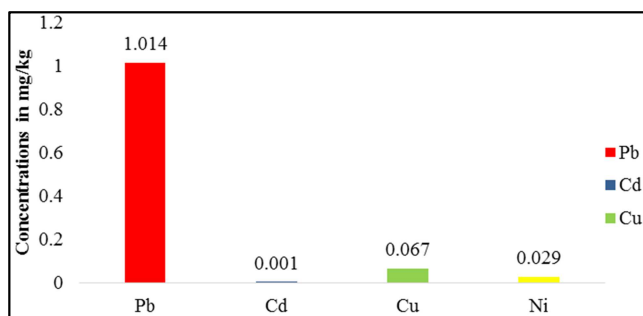


Figure 4. Heavy metal concentration (mg/kg) in *Crassostrea* spp. (oysters) at site A.

4.2.2. Site B

The concentration of Pb in site B varied from 1.031-1.037 mg/kg with mean level 1.033 ± 0.003 mg/kg; this is slightly higher than the FAO [11] permissible limit of 1.0 mg/kg, (Table 1 and Figure 5); Cd ranged from 0.001-0.005mg/kg with mean concentration of 0.003 ± 0.002 mg/kg which is below the FAO [11] limit of 1.0 mg/kg; Cu levels varied from 0.033-0.051mg/kg with mean concentration of 0.045 ± 0.010 mg/kg, this is below the FAO [11] permissible limit of 30.0 mg/kg. Ni ranged from 1.023-1.029 mg/kg with mean value of 1.027 ± 0.003 mg/kg.

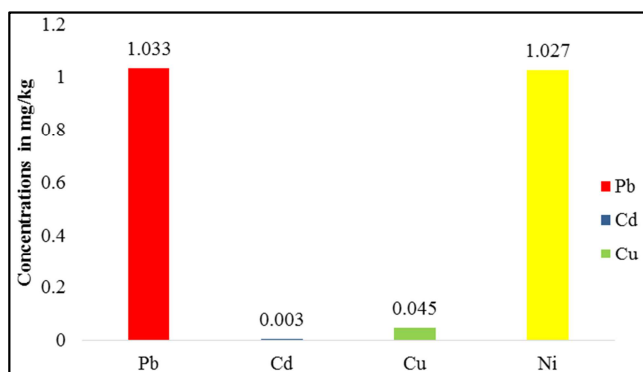


Figure 5. The heavy metal concentration (mg/kg) in *Crassostrea* spp. (oysters) at site B.

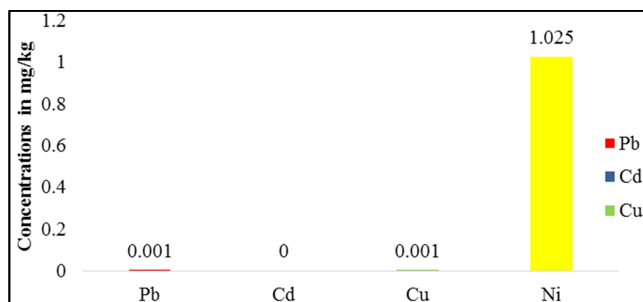


Figure 6. The heavy metal concentration (mg/kg) in *Crassostrea* spp. (oysters) at site C.

4.2.3. Site C

The levels of Pb in site C varied from 0.001-0.002 mg/kg, with mean concentration 0.001 ± 0.001 mg/kg which is below the FAO [11] limit of 1.0 mg/kg (Table 1 and Figure 6), Cu range from 0.001-0.002 mg/kg with mean concentration of 0.001 ± 0.001 mg/kg which is lower than the [11] permissible

limit of 30.0 mg/kg, Ni concentration ranged from 1.023-1.027 mg/kg with mean concentration of 1.025 ± 0.002 mg/kg.

4.3. Total Hydrocarbon

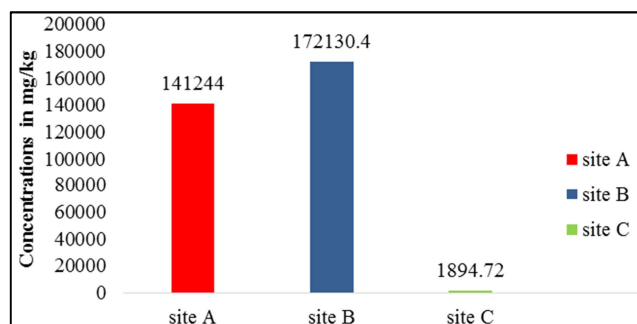


Figure 7. Total hydrocarbon content (mg/kg) in *Crassostrea* spp. (oysters) in the three study sites.

The concentration of total hydrocarbon content in oysters at site A ranged from 134,512.11-148,112.67 mg/kg with mean concentration of $141,244 \pm 6801.312$ mg/kg (Table 2 and Figure 7), The observed values from site B varies from 144,976.08-196,082.10 mg/kg with mean concentration of 172130.4 ± 25703.1 mg/kg, the concentration at site C was between 1810.09-1996.00 mg/kg with mean levels of 1894.73 ± 94.064 mg/kg.

4.4. Discussion

4.4.1. Heavy Metal Concentration in Site A

The highest level of heavy metals observed in site A, where Pb had a mean concentration of 1.014 ± 0.011 mg/kg followed by Cu (0.0627 ± 0.0829 mg/kg), Ni (0.0289 ± 0.006 mg/kg) and Cd (0.001 ± 0.001 mg/kg). Trace metals follows the trend of $Pb > Cu > Ni > Cd$. The EDI of oyster consumption in site A: for Pb was 2.589mg/kg, Cd (0.003 mg/kg), Cu (0.171 mg/kg) and Ni (0.072 mg/kg). According to Table 4, THQ of Pb was 2.7795, Cd (0.0096), Cu (0.0174) and Ni (0.0005), which were less than 1 except Pb that is greater than 1 and implying that the oysters were not safe for consumption. Lead, which was the most prominent trace metal at sites A and B is known to cause a neurological deficit such as mental retardation in children and kidney disease such as interstitial nephritis to adults and also contribute to hypertension and cardiovascular disease to the consumers in these coastal areas after long term consumption [29]. However, the observed values for metals were below FAO [11] limit of 1.0mg/kg for Pb, 1.0mg/kg for Cd and 30mg/kg for Cu. The observed value for Pb concentration were slightly above the limit, highlighting the need for adequate monitoring.

This lead result was in line with the study by Gongora-Gomez *et al* [12, 9] who assessed the concentrations of heavy metals in cultivated oysters from a farm located on the southeastern coast of the gulf of California using Atomic Absorption Spectrophotometer. Oysters samples were analyzed monthly (March – December 2011) for copper (Cu), lead (Pb) and nickel (Ni). The result indicated that, Cu, Cr,

Cd and Pb levels were above the maximum permissible values and thus pose a threat on human health. They recommended that metal concentration must be monitored periodically. They opined that the metal burden could be influenced by anthropogenic activities such as agriculture and aqua culture surrounding the culture zone. Furthermore, according to Ubong [25]; Ubong *et al.* [27] in a study conducted on the quality of potable water sources at Eket Local Government Area in Akwa Ibom State revealed that, Lead in borehole water ranged from 0.039 – 0.382mg/l with a mean of 0.23 ± 0.15 mg/l. This was above acceptable National NAFDAC/SON and International (WHO); [22] limit of lead in potable water which was 0.01mg/l [15]. This implies that, water in the region was already polluted with lead. A study conducted by Ubong *et al.* [24] on the distribution of heavy metals in tissues of *Callinectes latimanus* from the New Calabar Rivers of Rivers State in Nigeria revealed that, the levels of lead in the sediments from the study sites were more than those found in all the tissues of the crab, thus a link possibly exist between sediment load and that of the crab. The concentrations of Lead in the water (1.0 – 7.0 μ g/l), were lower than those in both crab and sediments, but were however, higher than the FEPA and WHO [30] standard for drinking water. This also confirms that; the region was polluted with Lead.

4.4.2. Heavy Metal Concentration in Site B

Figure 5 shows that at site B, the highest metal of concentration was Pb with mean values of 1.033 ± 0.003 mg/kg followed by Ni (1.027 ± 0.003 mg/kg), Cu (0.045 ± 0.010 mg/kg) and Cd (0.003 ± 0.002 mg/kg). According to Table 4. the EDI of oysters at site B were Pb (2.655 mg/kg), Cd (0.008 mg/kg), Cu (0.116 mg/kg), Ni (2.640 mg/kg). The total hazard quotient of Pb (2.8316) was the highest followed by Ni (0.4927), Cu (0.01167) and Cd (0.0288). The THQ result was below 1 for Cu, Cd and Ni while Pb is more than 1 and as such the oysters were not safe for consumption. Lead level which was the highest heavy metal at site. However, according to the study done by Jorge *et al*; 2015 the levels of six heavy metals in different clam species from 34 sites of Malaysian coast ranged as 0.18-8.51 mg/kg, 0.13-17.20 mg/kg, 2.17-7.80 mg/kg, 0.84-36.00 mg/kg, 24.13-38.00 mg/kg and 177.82-1912.00 mg/kg for Cd, Pb, Ni, Cu and Fe respectively. It was observed that the concentrations of metals slightly depended on different clam species but mostly depends on site locations. According to Malaysian food regulation (1985) about 30% and 50% were safe from Cd and Pb contamination respectively and also the clam species from the other populations studies were safe for consumption. The observed values of the heavy metals in site B for Pb is more than limit whereas others were below the permissible limit recommended by [11, 22] limit of 1.0mg/kg for Pb, 1.0mg for Cd and 30 mg/kg for Cu. Implying that consumption of the oysters will cause harmful effect on human and it followed the following trends Pb>Ni>Cu>Cd.

4.4.3. Heavy Metal Concentration in Site C (Control)

The highest concentration of heavy metal in site C (control)

was Ni with mean concentration of (1.025 ± 0.002 mg/kg) followed by Cu (0.001 ± 0.001 mg/kg), Pb (0.001 ± 0.001 mg/kg) and Cd had concentration that was below the detection limit of the equipment used. In EDI consumption of oysters at site C (control), Ni (2.6346 mg/kg) has the highest consumption followed by Pb (0.003mg/kg), Cu (0.003 mg/kg) and Cd (0.00mg/kg). The total hazard quotient of Ni (0.4917) was the highest followed by Pb (0.0027) and Cu (0.0003) (Table 4). The THQ results from site C were below 1 and as such the oysters were safe for consumption. It was observed that heavy metals at site C have the least concentration. Ni being the most concentrated heavy metal has no definite safety limits but high values may lead to serious health problems, including respiratory system cancer, and it can also cause a skin disorder known as nickel-eczema.

A similar investigation is the studies by Alavian [3]; Ikpe [14, 16] where 200 oysters were collected and their age was determined, then they were classified into four age categories and 15 oysters from each category were selected. Results of heavy metal analysis revealed that the accumulation of Ni and Pb in one-year old oysters (immature) was more than those in mature oysters (two, three and four-year-old oysters). Significant differences were observed between concentrations of Ni and Pb in mature and immature oysters. The results suggested that aging has a negative effect on bioaccumulation of Ni and Pb in *S. cucullata*; while it has no effect on bioaccumulation of Cd.

The observed values of all the trace metals assessed at site C in this study were below the [11] permissible limit of 1.0mg/kg for Pb, 1.0mg for Cd and 30 mg/kg for Cu. This implies that the oyster when eaten, will not cause any harmful effect on human. Generally the heavy metal concentration in *Crassostrea* spp. (oysters) obtained in site C followed the trends Ni > Pb > Cu > Cd. This observation differs with site A and Site B, where Pb recorded the highest concentration in the oyster analysis. Furthermore, heavy metal content was least in site C compared to site A and B, indicating minimal pollution status of site C with reference to site A and B.

4.4.4. Total Hydrocarbon Content

Figure 7 shows the level of total hydrocarbon content in oysters at the three different sampling sites. The levels of THC in site B (172130.4 ± 25703.1 mg/kg) was higher than site A ($141,244 \pm 6801.312$ mg/kg) and site C (1894.73 ± 94.064 mg/kg). This implies that the oysters accumulated more hydrocarbons in site B than site A and site C, indicating, a high level of pollution in the area. Hydrocarbons are not biodegradable and are therefore transported into the tissues of oysters via water intake. The high THC in *Crassostrea* spp. (oysters) obtained from site B may be due to the pollution of the area through oil spillage, since there were intensive oil exploration activities in the area. The THC recorded in site C (control) may be attributed to organic contaminants from human induced chemicals like pesticides, petrol (from automobiles) and other domestic wastes, since industrial activities were absent in site C. The

chemicals persist long enough in the environment to cause harmful effect. The contaminants tend to bio accumulate and bio magnify, exhibiting toxicity and other adverse outcomes like mutagenicity, carcinogenicity and teratogenicity resulting into chronic and acute disorders [7]; Ikpe *et al.*[13] However, site C (control) which are filled with organic contaminants still have the least mean concentration (Figure 7).

4.5. Statistical Analysis

4.5.1. Correlation Matrix

Correlation is the study of relationship between two data sets. If two sets of data are strongly linked together (high correlation) correlation has a value (-1 to 1), '1' means a perfect positive correlation, '0' means no correlation, '-1' is a perfect negative correlation.

Table 5 shows the correlation matrix between site A and B in which Pb shows a positive correlation with Cd and Ni, this implies that they are from the same source. Pb has a negative correlation with Cu which means that they are from different source. Pb and Cd show a positive correlation with all metals except with Cu that shows a negative correlation. Cu shows a negative correlation with Ni which means that it came from different source.

The significant positive correlation observed between metals at site A and site C (Table 6), and at site B and site C (Table 7) means that the metals in the site could have common sources. It was earlier pointed out by Sarbe *et al.* [20], Ogbeifun *et al.* [18] that when metals are released into the aquatic environment, they do not always remain in water column but could also be absorbed onto the sediment. Also the presence of these heavy metals in the soil and crop plant is due to the mobility of these metals from water to the farmlands around particularly through leaching and runoffs.

Table 5. Correlation matrix for site A and site B.

	Pb	Cd	Cu	Ni
Pb	1			
Cd	1	1		
Cu	-1	-1	1	
Ni	1	1	-1	1

Table 6. Correlation matrix for site A and site C.

	Pb	Cd	Cu	Ni
Pb	1			
Cd	1	1		
Cu	1	1	1	
Ni	-1	-1	-1	1

Table 7. Correlation matrix for site B and site C.

	Pb	Cd	Cu	Ni
Pb	1			
Cd	1	1		
Cu	1	1	1	
Ni	1	1	1	1

4.5.2. Statistical Analysis Using T-Test

Two-Sample Assuming Equal Variances between the

sampling sites summarily showed that, there was no significant difference between sites when $p > 0.05$ and thus implies there is no significant difference between the means of the study sites.

5. Conclusion

This study has revealed that the area under investigation was contaminated with heavy metals and total hydrocarbon content. The trend of heavy metal concentrations in site A and site B was $Pb > Ni > Cu > Cd$ while site C (control) was $Ni > Cu > Pb > Cd$. Total hydrocarbon content was highest in oyster in site B while site C recorded the least THC concentration. The total hazard quotient of heavy metals in the oysters assessed were less than 1 for Ni, Cd, Cu while the value for Pb was greater than 1 for sites A and B, thus implying that the oysters were not safe for consumption. THQ for site C were less than 1 indicating that the oysters do not pose an appreciable hazard to humans with respect to heavy metals levels. The observed values of the heavy metals in site B and A for Pb were more than limit whereas others were below the permissible limit recommended by FAO [11] of 1.0mg/kg for Pb, 1.0mg for Cd and 30mg/kg for Cu. Implying that consumption of the oysters will cause harmful effect on human. The heavy metal levels in the oysters were below the permissible limit of 1.0mg/kg for Pb, 1.0mg for Cd and 30mg/kg for Cu by FAO [11] at site C. The result from the studies revealed that site C (control) had the least heavy metals and THC concentration, indicating a very minimal pollution of the area. Statistically there was no significant difference because the P-value was greater than alpha ($p > 0.05$). The THQ result for sites A and B were below 1 for Cu, Cd and Ni while Pb was more than 1 indicating that the oysters were not safe for consumption. The THQ results from site C were below 1 and as such the oysters were safe for consumption.

References

- [1] Abha, S., and Singh, C. S. (2012). Hydrocarbon Pollution: Effects on Living Organisms Remediation of Contaminated Environments, and Effects of Heavy Metals Co-Contamination on Bioremediation In Introduction to Enhanced Oil Recovery (EOR) Processes and Bioremediation of Oil-Contaminated Sites. Institute of Microbial Technology, Chandigarh, India. Available on line at www.intechopen.com.
- [2] Agusa, T., Kunito, T., Sudaryanto, A., Monirith, I and Iwata, H (2007). Exposure assessment for trace elements from consumption of marine shell fish in Southeast Asia. *Environ Poll* 145 (3): 766-777.
- [3] Alavian, Petroody S. S., Hamidian, A. H., Ashrafi, S., Eagderi, S and Khazaei, M. (2016) "Study on age-related bioaccumulation of some heavy metals in the soft tissue of rock oyster (*Saccostrea cucullata*) from Laft Port – Qeshm Island, Iran" *Iranian Journal of Fisheries Sciences* 16 (3) 897-906 2017.
- [4] AOAC (1995). Official method of analysis, 16th Edition, Association of Analytical Chemist. Arlington Virginia, 4: 1-16.

- [5] AOAC (2000), official method of Analysis, 17th edition, Association of Analytical Chemist. Gaithersburg, MD, USA. 624-642.
- [6] Bahr, L. M., Lanier, W. P., (1981). The ecology of intertidal oyster reefs of the South Atlantic Coast: a community profile. U. S. Fish and Wildlife Service Program FWS/OBS/ -81/15, pp. 105.
- [7] Barnes, K. K., Kolphin, D. W., Furlong, E. T., Meyer, M. T. and Barber, L. B. (2008) "A national reconnaissance of pharmaceuticals and other organic waste contaminants in the United States".
- [8] Chiu W. C. and Cheng D. D. (2012) Determination of Hydrocarbons in industrial harbor Sediments and marine organisms by GC-MS. Int. J. Environ. Res. Public Health.
- [9] Clinton, I. H., Ujagwung, U. G. and Horsfall, M. (2008). Evaluation of total hydrocarbon levels in some aquatic media in an oil polluted mangrove Wetland in the Niger Delta. Vol. 9 (3) 593 – 661.
- [10] Ekanem, A. E., Ikpe, E. E. Ekwere, I. E. (2019). Assessment of polycyclic aromatic hydrocarbon in soil around automobile repair workshops within Eket metropolis, Akwa Ibom State, Nigeria. International journal of research and scientific innovation. Vol. 6, issue 1, 102- 107.
- [11] FAO (Food and Agriculture Organization), 2003. Retrieved 2012. From Heavy Metal Regulations Faolex: <http://faolex.org/docs/pdf/eri42405.pdf>
- [12] Góngora-Gómez A. M., García-Ulloa, M., Muñoz-Sevilla, P. N. and Domínguez-Orozco, A. L. (2017). Heavy-metal contents in oysters (*Crassostrea gigas*) cultivated on the southeastern coast of the Gulf of California, Mexico. Hydrobiological 27 (2): 219-227.
- [13] Ikpe, E. E. Ekwere, I. O., Ukpog, E. G., Effiong, J. O., Okon, O. E. (2019). Evaluation of the levels of heavy metals and total hydrocarbon content in *Tympanotomus fuscatus* and sediment, Qua-Iboe River, Akwa Ibom state, Nigeria. Chemical science International journal. Vol. 27, issue 4, 1-17.
- [14] Ikpe, E. E., Ubong, U. U. and Archibong, U. D. (2022). Proximate analysis, heavy metals hydrocarbon content of *Callinectes sapidus* obtained from Ibaka River, Akwa Ibom State, Nigeria. JEJOST.
- [15] IPAN, 2005. Institute of Public Analyst of Nigeria. Water and Waste water Analysis. Paper Presented in Pre-Admission Training Workshop on Food, Drugs, Cosmetics, Medical Devices, Water, Environment and Petroleum.
- [16] Jorge, R., Ruelas-Inzunza, M. D. Faruk, H., (2015) Heavy metals in different clam species from 34 sites of Malaysian Coast.
- [17] Li, J., Liu, G., Yin, L., Xue, J., Qi, H. and Li, Y. 2013. Distribution Characteristics of Total Hydrocarbons in Sediments and Biota from Zha Long Wet Land, China. Environmental monitoring assessment, 185: 3163-3171.
- [18] Ogbeifun, D. E., Archibong, U. D., Chiedu, I. E. Ikpe, E. E. (2019). Assessment of the water quality of Boreholes in selected areas in Benin city, Edo state, Nigeria. Chemical science international Journal. Vol. 28 (2) 1-13.
- [19] Onen, S., Kucuksezgin, F. and Kocak, F. 2011. Temporal And Spatial Bio monitoring of HeavyMetals in Eastern Aegean Costal Waters Using Amphitrite. Air pollution bulletin, 62: 2548-2556.
- [20] Sarbe, A., Navjaya, A. J. and Galadima, A. I. (2008)" Assessment of some heavy metals in water, sediment and fresh shell fish from river Gongola in Yamaltu, Gombe, Nigeria". International Journal of Pure and Applied Chemistry.
- [21] Schwapp, A. P., Su J., Wetzel, S., Pekarek, S. and Banks, M. K. (1999). Extraction of petroleum hydrocarbon from river by mechanical shaking. Environ. Sci. Technol., 33: 1940-1945.
- [22] United State Environmental Protection Agency USEPA. 1987. Technical Guidance for Hazard Analysis. U.S. Environmental Protection Agency, Washington D. C.
- [23] US-EPA IRIS (2006). United States, Environmental Protection Agency, Integrated Risk Information System. <<http://www.epa.gov/iris/subst>>.
- [24] Ubong, U. U., Horsfall, M. and Ubong, I U. (2011) Distribution of heavy metals in tissues of *Callinectes latimanus* from the NEW Calabar River Nigeria. Afr J. Environ. Pollut. Health 9 (i): 7-13 "2011" ISSN = 1596-7425.
- [25] Ubong, U. U., Ubong, I. U. Ubong, E. U., Etukudoh, O. U. (2015). Assessment of Quality of Potable water sources in Eket Local Government Area of Akwa Ibom State, Nigeria. International Journal of Advanced and Innovative Research (2278-7844) #136/volume 4 Issue 8.
- [26] Ubong, U. U., and Ekwere, I. O. (2022). Distribution and human health risk Assessment of heavy metals in tissue of *Callinectes sapidus* from Iko River, Akwa Ibom state, Nigeria. Asian journal of Environment and Ecology. 19 (3).
- [27] Ubong, U. U., Ekwere I. O., Ikpe, E. E. and Obadimu C. O. (2022). Heavy metals and total hydrocarbon grown along shores of Qua- Iboe River, Akwa Ibom State, Nigeria. Chemical science international journal. Vol. 31, issue 5, 11-18.
- [28] Ubong., U. U., Ekwere, I. O., Obadimu, C. O. and Uwanta, E. J (2023) Pollution Status of Dumpsites within Uyo Metropolis, Akwa Ibom State. Journal of Geography, Environment and Earth Science International. Vol. 27, issue1, 1-10.
- [29] WHO (World Health Organization), Lead: International Programme on Chemical Safety (IPCS), WHO Food Additives Series 44, World Health Organization, Geneva, Switzerland, 2000.
- [30] WHO, (2008). Guideline for drinking water quality, 3rd ed. Incorporating 1st and 2nd Addenda. Vol. 1: Recommendation. Geneva: World Health Organization.