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Heavy Metals and PAHs Levels in Aquatic Organisms (Crab, Fish and Crayfish) from Crude Oil Polluted Rivers (Ekpan and Ogunu Rivers), Warri, Delta State, Nigeria

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Abstract

The purpose of this work was to determine level of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in aquatic organisms from crude oil polluted rivers in Warri, Delta State (Ekpan and Ogunu communities) and non-oil exploration site (Agbarho). The aquatic animals (crabs, fish, and crayfish) collected were washed, oven dried separately and homogenized in a blender and stored for analysis. Three replicates of each sample collected were used for analysis. PAHs were determined by Gas Chromatography (GC) with Flame Ionization Detector (FID) while heavy metal contents were determined by Atomic Absorption Spectrophotometer. The results revealed that the aquatic organisms from Ogunu and Ekpan had high levels of heavy metals and PAHs. The heavy metal contents such as Cadmium, Zinc, Chromium, Mercury, Copper, and Lead of the samples from Ogunu were found to be higher compared to those of Agbarho and Ekpan at $p<0.05$. The highest levels of PAHs in crabs were found in samples from Agbarho and Ekpan with little significant difference. In fish sample, the highest levels of PAHs were found in samples from Ogunu (0.0244 mg/kg) while the least was found in fish samples from Agbarho (0.014 mg/kg). PAHs levels in crayfish samples was higher in samples from Ogunu. The study generally suggests that samples from Ekpan and Ogunu communities are polluted compared to those from Agbarho with some certain exceptions. The order of pollution was found to be in the following order Ogunu>Ekpan>Agbarho.

Keywords: *Aquatic foods, heavy metals, polycyclic aromatic hydrocarbons (pahs), crude oil polluted rivers.*

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1. Introduction

The aquatic environment is a dynamic and nonetheless a diverse network of habitats and species, governed by complex physical and ecological processes that interact with humans and their activities at many levels. It acts like a large sink and takes in all it receives and then gives back in a way that could be beneficial or harmful (Bayowa and Agbozu, 2016). Again the natural environment has a way of cycling substances around it in such a way that every part is affected directly or indirectly by the consequence of the usage of another (Botkin and Keller, 2005). The benefits that humans receive from these habitats and communities are referred to as ecosystem services. The more obvious of these are the fish, shellfish and other foods that we consume, and the recreational or aesthetic benefits we derive from the sea. Apart from the beneficial seafoods, the aquatic environment is a reservoir of crude oil - petroleum derived from plant material and animals that originated millions of years ago, and have been modified over time by heat and pressure underground.

Crude oils are complex mixtures of hydrocarbons, with small amounts of other compounds and elements that typically include sulphur and other trace elements. Nowadays, due to the increasing need to generate income from natural resource exploration such as from crude oil export, there has been often oil spills to the environment. The carelessness of the oil industry in Nigeria Niger Delta region has precipitated this situation, which can perhaps be best encapsulated by a 1983 report issued by the Nigeria national petroleum corporation long before popular unrest surfaced. Reports on the extent of the oil spills vary. The Department of Petroleum Resources estimated 1.89 million barrels of petroleum were spilled into the Niger Delta between 1976 and 1996 out of a total of 2.4 million barrels spilled in 4,835 incidents, approximately 220 thousand cubic metres (Vidal, 2010). United Nations Development Programme report (2006) states that there have been a total of 6,817 oil spills between 1976 and 2001, which account for a loss of three million barrels of oil, of which more than 70 % was not recovered. A breakdown report states that 69 % of these spills occurred off-shore, a quarter was in swamps and 6 % spilled on land. These wanton spills may have introduced devastating pollutants such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals to the environment.

Heavy metals are one of the major threats for fish consumers and the effects on the contamination of fishing products becomes now a serious issue to be addressed especially with the increasing cases of metabolic diseases. The metal contaminants in aquatic systems usually remain either in soluble or suspension form and finally tend to settle down to the bottom or are taken up by the organisms (Reddy *et al*., 2007). Heavy metal contamination may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organisms (Ashraj, 2005; Vosyliene and Jankaite, 2006). Among heavy metals, Cd (II), Cr (VI), Cu (II), Pb (II) and Zn (II) have attracted lots of attention of researchers because they are widely spread in environment, and some of them are necessary to plants in small amount but turn out to be hazardous in slightly larger amount than the required consistence (Zhang *et al*., 2016).

On the other hand, polycyclic aromatic hydrocarbons (PAHs) are a class of chemicals that occur naturally in coal, crude oil, and gasoline. They are also produced when coal, oil, gas, wood, garbage, and tobacco are burned. PAHs are very well known for their carcinogenic properties. They are hydrophobic in nature and their persistence in the environment is mainly due to their low water solubility and electro-chemical stability. Evidence suggest that the lipophilicity, environmental persistence and genotoxicity of PAHs increases as the molecular size of the PAHs increases up to four or five fused benzene rings (Cerniglia, 1984).

2. Literature Review

Pollution is a global problem and the dangers and risks associated with it on human health is great. The impact of pollution in the vicinity of overcrowded cities and from industrial effluents and automobiles has reached a disturbing magnitude and is arousing public awareness (Begum *et al*., 2009). Excessive levels of pollutants are causing a lot of damages to human and animal health, plants including tropical rain forests as well as the wider environment (Khan and Ghouri, 2011). Pollution is one of the cause of many diseases, which affect not only the old but also the young and the energetic and all animals and plants (Kanmony, 2009). The World Health Organization (WHO) report points out that twenty million children worldwide suffer from pollution which has become critical because of overpopulation (Kanmony, 2009; Pain, 2008). An estimated 1.2 billion people drink unclean water which is the source of water related diseases that kill between five-ten million people mostly children around the world (Ahuja, 2009).

The natural substances which cause water pollution include, gases, oils, minerals, humus materials, waste created by animals and other living organisms present in water. Estimation indicates that more than fifty countries of the world with an area of twenty million hectares' area have polluted environment or partially polluted water including parts of all continents and this poor quality water causes health hazards and death of human beings, aquatic life and also disturbs the production of different crops (Khan and Ghouri, 2011).

Polycyclic aromatic compounds include different groups of compounds which have two or more benzenoid groups in their structure and various functional groups which may contain several elements. An important group of polycyclic aromatic compounds are the polycyclic aromatic hydrocarbons (PAHs) which have two or more fused benzonoid rings and no elements other than carbon and hydrogen (Henner *et al*., 1997). They may be eliminated or transformed to even more toxic compounds by chemical reactions such as sulfonation, nitration or photooxidation. For instance, in some conditions, traces of nitric acid can transform some PAHs into nitro-PAHs. It has been estimated that stationary sources contribute approximately 90 % of total PAH emission, but this is not true in urban and suburban areas, where the mobile sources are prevailing. The highest concentrations of atmospheric PAH can be found in the urban environment, due to the increasing vehicular traffic and the scarce dispersion of the atmospheric pollutants. The risk associated with human exposure to atmospheric PAH is highest in the cities, considering the density of population (Caricchia *et al*., 1999). Another most common environmental pollutants in the world are heavy metals (Papatilippaki *et al.,* 2008). The presence of heavy metals at trace level and essential elements at elevated concentration causes toxic effects if exposed to human population (Fong *et al*., 2008). The accumulation of heavy metals in agricultural soils is of increasing concern due to food safety issues and potential health risks as well as its detrimental effects on soil ecosystems (Qishlaqi and Moore, 2007). Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air (Begum *et al*., 2009). Metal poisoning arise from heavy metals that have toxic properties leading to adverse effects on human and ecosystem health (Voet *et al*., 2008).

3. Materials and Methods

3.1 Sample Collection

The samples (crab, fish and crayfish) were obtained from the sampling communities (crude oil polluted rivers in Warri, Delta State (Ekpan and Ogunu communities) and non-oil exploration site (Agbarho). The seafoods were identified and preserved in an ice bag below 4 ºC in an acid washed plastic container while transporting them to the laboratory for analysis.

3.2 Sample preparation

The water sample and sediments were placed in an airtight container. Seafoods collected were washed, oven separately and homogenized in a blender and stored for analysis. Three replicates of each sample collected were used for analysis.

3.3 Heavy Metal Analysis

Digestion was done using Nitric acid (HNO_3) and Perchloric acid ($HClO_3$) at the ratio of 6:3. Half a gram (0.5 g) of the sample was added into 250 ml conical flasks, followed by 6 ml of nitric acid (HNO_3) and 3 ml of Perchloric acid ($HClO_3$). The solution was swirled and heated at temperature of 120˚C for 10 minutes. Boiling chips was used as anti-bubbling agent to reduce the bubbling effects of the boiling solution. Upon heating, brown fumes of nitric acid (HNO_3) appeared first, followed by white frost which indicated the end of digestion. The solution was allowed to cool at room temperature and then filtered using Whatman filter paper. The filtrate was placed into appropriately labelled calibrated plastic container and made up to mark (50 ml) with distilled water. The container was corked and shelved for analysis. The digested samples were subjected to analysis using the Atomic Absorption Spectrophotometer (GBC Avanta Ver 2.20 equipped with lamp).

3.4 PAH Determination

Liquid-liquid extraction methods were used for the extraction of PAHs in water samples. Seventy-five grammes (75g) of NaCl was added to 500 mL of the sample in a separating funnel. PAHs in the sample was extracted three times using a mixture of dichloromethane and n-hexane. After vigorous shaking, the extract was dehydrated using anhydrous sodium sulfate, and concentrated to 2.0 mL with a rotary evaporator at 35–40 ˚C. The extraction solutions were loaded and aspirated through the cartridge under gentle vacuum at a flow rate of less than 2 mL/min. The collected extract was reconstituted in 1 mL n-hexane and analysed. PAHs analysis were carried out using Gas Chromatography (GC) with Flame Ionization Detector (FID).

3.5 Statistical Analysis

Statistical analysis were performed using Statistical Package for Social Sciences (SPSS) software. One way analysis of variance (ANOVA) was used to compare differences in mean result of different sample groups. Results were expressed as mean ± standard deviation (Mean ±SD) of three different replicate determinations.

4. RESULTS

4.1 Heavy metal contents

4.1.1 Heavy metal level in crabs from crude oil exploration communities

The concentration of heavy metals in crabs from rivers in crude oil exploration communities of Delta State were presented in Table 1.
The result shows that Ogunu had the highest levels of Zn (0.46 ± 0.01^a mg/kg). The levels of Cd and Cu were below detectable limits. There is no significant difference in mean of Cr for crab samples from all three locations at $p<0.05$.
The highest levels of Pd was found in crabs from Agbarho (0.03 ± 0.00^amg/kg) and Ekpan (0.03 ± 0.002^amg/kg) which is not statistically significant at $p<0.05$.

Table 1. Heavy metals levels of crabs from rivers in crude oil exploration communities of Delta State (mg/kg)

Heavy metals	Agbarho	Ogunu	Ekpan
Cd	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}
Zn	0.38 ± 0.02^{b}	0.46 ± 0.01^{a}	0.39 ± 0.01^{b}
Cr	0.02 ± 0.01^{a}	0.02 ± 0.00^{a}	0.03 ± 0.00^{a}
Cu	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.0 ± 0.00^{a}
Pb	0.03 ± 0.01^{a}	0.00 ± 0.00^{a}	0.03 ± 0.002^{a}

Values are mean ± SD of triplicate determination values within the same row bearing the same superscript letters are not significantly different at $p< 0.05$.

4.1.2 Heavy metal level in fish from crude oil exploration communities

The concentration of heavy metals in fish samples from rivers in crude oil exploration communities of Delta State were presented in Table 2.

The result shows that Ogunu had the highest levels of Zn (0.17 ± 0.01^{a} mg/kg) and Pb (0.06 ± 0.01^{a}mg/kg). The levels of Cd and Cu were below detectable limits in fish samples from Agbarho and Ekpan. There is no significant difference in mean of Hg for fish samples from all three locations at $p<0.05$. The highest levels of Cd was found in fish from Ogunu (0.02 ± 0.00^{a}mg/kg) which is not statistically significant at $p< 0.05$.

Table 2. Heavy metals levels of fish from rivers in crude oil exploration communities of Delta State (mg/kg)

Heavy metals	Agbarho	Ogunu	Ekpan
Cd	0.00 ± 0.00^{b}	0.02 ± 0.00^{a}	0.00 ± 0.00^{b}
Zn	0.14 ± 0.41^{b}	0.17 ± 0.01^{a}	0.016 ± 0.01^{a}
Cr	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.02 ± 0.01^{a}
Hg	0.01 ± 0.01^{a}	0.01 ± 0.01^{a}	$0.01\pm0.00^{a\,b}$
Cu	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}
Pb	0.03 ± 0.01^{b}	0.06 ± 0.01^{a}	0.04 ± 0.016^{b}

Values are mean ± SD of triplicate determination values within the same row bearing the same superscript letters are not significantly different at < 0.05.

4.1.3 Heavy metals level in crayfish from crude oil exploration communities

The concentration of heavy metals in crayfish samples from rivers in crude oil exploration communities of Delta State were presented in Table 3

The result shows that Ogunu had the highest levels of Cd, Zn (0.23 ± 0.01^{a}mg/kg) and Cr (0.06 ± 0.01^{a}mg/kg). The levels of Cu were below detectable limits in crayfish samples from all three locations. There is no significant difference in mean of Hg for fish samples from Agbarho (0.01 ± 0.00^{a}mg/kg) and Ekpan (0.01 ± 00.0^{a} mg/kg) locations at $p<0.05$. The highest levels of Pb was found in fish from Ogunu (0.04 ± 0.02^{a}mg/kg) and Ekpan (0.04 ± 0.02^{a}mg/kg) which is not statistically significant at $p<0.05$.

Table 3. Heavy metals levels of crayfish from rivers in crude oil exploration communities of Delta State (mg/kg)

Heavy metals	Agbarho	Ogunu	Ekpan
Cd	0.00 ± 0.00^{a}	0.01 ± 0.01^{a}	0.00 ± 0.00^{a}
Zn	0.17 ± 0.01^{b}	0.23 ± 0.01^{a}	0.17 ± 0.03^{b}
Cr	0.01 ± 0.00^{c}	0.06 ± 0.00^{a}	0.02 ± 0.00^{b}
Hg	0.01 ± 0.00^{a}	0.02 ± 0.00^{a}	0.01 ± 00.0^{a}
Cu	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}
Pb	0.02 ± 0.00^{a}	0.04 ± 0.02^{a}	0.04 ± 0.01^{a}

Values are mean ± SD of triplicate determination values within the same row bearing the same superscript letters are not significantly different at $p< 0.05$.

4.2 Polycyclic Aromatic Hydrocarbon Content

4.2.1 Polycyclic aromatic hydrocarbon content in the crab samples

The result obtained from the determination of the polycyclic aromatic hydrocarbons (PAHs) contents of the crab samples were presented in Table 4. The result indicates the presence of low molecular weight (LMW) PAHs such as Fluorene (0.001 mg/kg), Naphthalene (0.001 mg/kg) and phenanthrene (0.009 mg/kg) in crab samples from Agbarho while Acenaphthene and Acenaphthylene were absent. Phenanthrene was found in crabs from all three communities which indicates it persistence. The subtotal of LMW PAHs followed this order, Ogunu (0.033 mg/kg)> Ekpan (0.013 mg/kg)>Agbarho (0.011 mg/kg).

The medium molecular weight (MMW) PAHs (Flouranthene and Pyrene) were investigated. The result shows that Flouranthene was present in crab samples from Ekpan (0.001 mg/kg) and Ogunu (0.001 mg/kg) whereas it was absent in samples from Agbarho. Pyrene was absent in Ogunu but present in Agbarho (0.003 mg/kg) and Ekpan (0.001 mg/kg). The subtotal MMW mean followed this order Agbarho (0.003 mg/kg)> Ekpan (0.002 mg/kg)>Ogunu (0.001 mg/kg).

High molecular weight (HMW) PAHs (Dibenzyl(g-h)anthralene, 1,2-benzanthracene, Benzo (g) pyrence, Benzo (g-h-i) perylene, Benzo(b) fluoranthene, Benzo (k) fluoranthene, Xylene) were investigated. The result indicates the presence of Dibenzyl(g-h)anthralene (0.002 mg/kg), Benzo (g) pyrence (0.017 mg/kg), Benzo (g-h-i) perylene (0.001 mg/kg), Benzo(b) fluoranthene (0.006 mg/kg) in crab samples from Ogunu. The PAH, 1,2-benzanthracene was absent in crab samples from Ekpan and Ogunu. The subtotal of HMW was found to be higher in crab samples from Ogunu (0.01 mg/kg) when compared to Agbarho (0.008 mg/kg) and Ekpan (0.007 mg/kg) at $p<0.05$.

The sum total of PAHs contents were found to be higher in crab samples from Ogunu (0.012 mg/kg) with no difference in mean for Agbarho (0.022 mg/kg) and Ekpan (0.022 mg/kg).

Table 4. Polycyclic aromatic hydrocarbon (PAHs) contents of the crab samples (mg/kg)

PAHs components	**Agbarho**	**Ekpan**	**Ogunu**
Fluorene	0.001	0.004	-
Naphthalene	0.001	-	0.02
Phenanthrene	0.009	0.008	0.013
Acenaphthene	-	0.001	-
Acenaphthylene	-	-	0.001
Subtotal of LMW	**0.011**	**0.013**	**0.033**
Pyrene	0.003	0.001	-
Flouranthene	-	0.001	0.001
Subtotal of MMW	**0.003**	**0.002**	**0.001**
1-2 benzanthracene	0.002	-	-
Benzo (g) pyrence	0.005	-	0.017
Benzo (g-h-l) perylene	0.001	-	0.001
Benzo(b) fluoranthene	0.000	0.001	0.006
Dibenzyl(g-h)anthralene	-	0.006	0.002
Xylene	-	-	0.001
	-	-	
Subtotal of HMW	**0.008**	**0.007**	**0.010**
∑PAHs	0.022	0.022	0.012

4.2.2 Polycyclic aromatic hydrocarbon content in the fish samples

The result obtained from the determination of the polycyclic aromatic hydrocarbons (PAHs) contents of the fish samples were presented in Table 5. The result indicates the presence of low molecular weight (LMW) PAHs such as Fluorene (0.003 mg/kg), Naphthalene (0.001 mg/kg) and Acenaphthene (0.009 mg/kg) in fish samples from Ekpan while Phenanthrene and Acenaphthylene were absent. Agbarho had only Phenanthrene (0.003 mg/kg), and Naphthalene (0.001 mg/kg) while fish samples from Ogunu had Phenanthrene (0.013 mg/kg) and Acenaphthylene (0.001 mg/kg) . The subtotal of LMW occurred in the following order, Ogunu (0.014 mg/kg)> Ekpan (0.005 mg/kg)>Agbarho (0.004 mg/kg).

The medium molecular weight (MMW) PAHs (Flouranthene and Pyrene) were investigated. The result shows that Flouranthene was present in fish samples from Agbarho while Ekpan had the same mean concentration of 0.001 mg/kg with Ogunu (0.001 mg/kg) whereas it was absent in samples from Ogunu. Pyrene was absent in Ogunu but present in Ekpan (0.001 mg/kg). The subtotal MMW mean indicated the following order Ekpan (0.002 mg/kg)>Agbarho (0.001 mg/kg)>Ogunu (0.000 mg/kg).

High molecular weight (HMW) PAHs (Dibenzyl(g-h)anthralene, 1,2-benzanthracene, Benzo (g) pyrence, Benzo (g-h-i) perylene, Benzo(b) fluoranthene, Benzo (k) fluoranthene, Xylene) were investigated. The result indicates the presence of Dibenzyl(g-h)anthralene (0.002 mg/kg), Benzo (g) pyrence (0.015 mg/kg), Benzo (g-h-i) perylene (0.001 mg/kg), Benzo(b) fluoranthene (0.004 mg/kg) and xylene (0.001 mg/kg) in fish sample from Ogunu. The PAH, 1,2-benzanthracene was absent in fish samples from Ekpan and Ogunu. The subtotal of HMW was found to be higher in fish samples from Ogunu (0.023 mg/kg) when compared to Agbarho (0.00 mg/kg) and Ekpan (0.01 mg/kg) at $p<0.05$. The sum total of PAHs contents were found to be higher in fish samples from Ogunu (0.0224 mg/kg)> Ekpan (0.017 mg/kg) >Agbarho (0.014 mg/kg).

Table 5. Polycyclic aromatic hydrocarbon (PAHs) contents of the fish samples (mg/kg)

PAHs components	Agbarho	Ekpan	Ogunu
Fluorene	0.000	0.003	-
Naphthalene	0.001	0.001	-
Phenanthrene	0.003	-	0.013
Acenaphthene	-	0.001	-
Acenaphthylene	-	-	0.001
Subtotal of LMW	**0.004**	**0.005**	**0.014**
Flouranthene	0.001	0.001	-
Pyrene	0.000	0.001	-
Subtotal of MMW	**0.001**	**0.002**	**-**
1-2 benzanthracene	0.002	-	-
Benzo (g) pyrence	0.004	-	0.015
Benzo (g-h-l) perylene	0.003	-	0.001
Benzo (b) fluoranthene	0.000	0.002	0.004
Dibenzyl (g-h) anthralene	-	0.008	0.002
Xylene	-	-	0.001
	-	-	
Subtotal of HMW	**0.009**	**0.010**	**0.023**
∑PAHs	0.014	0.017	0.0244

4.2.3 Polycyclic Aromatic Hydrocarbon content in the crayfish samples

The result obtained from the determination of the polycyclic aromatic hydrocarbons (PAHs) contents of the crayfish samples were presented in Table 6. The result indicates that there was the presence of low molecular weight (LMW) PAHs such as Fluorene (0.002 mg/kg), Naphthalene (0.001 mg/kg) and Phenanthrene (0.009 mg/kg) in crayfish samples from Agbarho while Acenaphthene was absent, Anthracene and Acenaphthylene. Phenanthrene was present in all three crayfish samples. Crayfish samples from Ekapan had Acenaphthene (0.006 kg/mg), Fluorene 0.005 mg/kg), and Phenanthrene (0.001 mg/kg). The subtotal of LMW indicates that Ogunu had the highest LMW PAHs (0.732 mg/kg) while no significant difference was observed in the mean of Agbarho (0.012 kg/mg) and Ekpan (0.012 kg/mg) at $p<0.05$.

The medium molecular weight (MMW) PAHs (Flouranthene and Pyrene) were investigated. The result shows that Flouranthene was present in crayfish samples from Ekpan (0.001 mg/kg) but below detectable limit in crayfish samples from Agbarho and Ogunu. Pyrene was present in samples from Ekpan but absent in samples from Ogunu. The subtotal mean levels were higher in Ekpan (0.002 mg/kg) and Ogunu (0.001 mg/kg).

High molecular weight (HMW) PAHs (Dibenzyl(g-h)anthralene, 1,2-benzanthracene, Benzo (g) pyrence, Benzo (g-h-i) perylene, Benzo(b) fluoranthene, Benzo (k) fluoranthene, Xylene) were investigated. The result indicates the presence of Benzo (g) pyrence (0.005 mg/kg), Benzo (g-h-i) perylene (0.001 mg/kg), 1,2-benzanthracene (0.001 mg/kg) in crayfish samples from Agbarho while Dibenzyl(gh)anthralene, Benzo (k)fluoranthene and Xylene were absent. The subtotal of HMW was found to be higher in crayfish samples from Ogunu (0.021 mg/kg) when compared to Agbarho (0.007 mg/kg) and Ekpan (0.006 mg/kg) at $p<0.05$.

The sum total of PAHs contents were found to be higher in crayfish samples from Ogunu (0.762 mg/kg)> Ekpan (0.02 mg/kg) >Agbarho (0.01 mg/kg,in the .order outlined above

Table 6. Polycyclic aromatic hydrocarbon (PAHs) contents of the crayfish samples (mg/kg)

PAHs components	Agbarho	Ekpan	Ogunu
Acenaphthene	-	0.006	-
Anthracene	-	-	0.71.920
Acenaphthylene	-	-	0.028
Fluorene	0.002	0.005	-
Naphthalene	0.001	-	-
Phenanthrene	0.009	0.001	0.012
Subtotal of lmw	**0.012**	**0.012**	**0.7396**
Pyrene	0.000	0.001	-
Flouranthene	-	0.001	0.001
Subtotal of mmw	**0.000**	**0.002**	**0.001**
1-2 benzanthracene	0.001	-	-
Benzo (g) pyrence	0.005	-	0.017
Benzo(g-h-l) perylene	0.001	-	-
Benzo(b)fluoranthene	0.000	0.001	0.001
Dibenzyl(gh)anthralene	-	0.005	-
Benzo (k)fluoranthene	-	-	0.002
Xylene	-	-	0.001
Subtotal of hmw	**0.007**	**0.006**	**0.021**
∑PAHs	0.019	0.020	0.762

5. DISCUSSION

Environmental pollution results from the introduction of harmful substances into the natural environment. These substances which are referred to as pollutants could be naturally occurring or artificially introduced. There are over hundreds of these toxic contaminants that have been identified (Chatterjea and Shinde, 2012). Its exposure and persistence in the natural environment can cause an upset which usually results to an imbalance in the biosphere when these toxic substances find its way into the ecosystem. These imbalances follows similar trend of transient of energy from the natural environment to producers and to consumers. The bioaccumulation of pollutants in seafoods is also worth investigating as this serves as source of livelihood and food reserves for residents within and outside the communities. Sea foods such as crabs, prawn, and fishes have since been known to bio accumulate pollutants, which on consumption over extended period of time could cause cancer and other life threatening diseases. To this effect, constant monitoring of the level of pollutants in the sea foods is worth investigating in order to avoid epidemic resulting from contaminated or polluted foods.

5.1 Heavy Metal Levels

Metals are a group of the most important pollutants which cause environmental degradation in coastal areas. Trace metals are introduced into the aquatic ecosystems in a number of ways. These chemicals accumulate in the tissues of aquatic organisms at concentrations many times higher than concentrations in water and may be biomagnified in the food chain to levels that cause physiological impairment at higher trophic levels and in human consumers (Raposo *et al*., 2009). Heavy metals are natural constituents of the Earth's crust and are present in varying concentrations in all ecosystems. During the past two decades, high levels of metals and their compounds, both inorganic and organic, have been released to the environment as a result of a variety of anthropogenic activities (Komarnicki, 2005). Trace metal bioaccumulation in food chain especially those with high toxicity can be highly dangerous to human health (Turkdogen *et al*., 2003). These metals enter the human body mainly through two route namely ingestion and inhalation. But the main route of exposure to this element in human population is ingestion.

The concentration of heavy metals in crabs shows that Ogunu had the highest levels of Zn (0.46±0.01mg/kg). The levels of Cd and Cu were below detectable limits. There is no significant difference in mean of Cr for crab sample in from all three locations at $p<0.05$. The highest levels of Pd was found in crabs from Agbarho (0.03±0.00mg/kg) and Ekpan (0.03±0.002mg/kg)which is not statistically significant at $p<0.05$. The concentration of heavy metals in fish samples shows that Ogunu had the highest levels of Zn (0.17±0.01mg/kg) and Pb (0.06±0.01mg/kg). The levels of Cd and Cu were below detectable limits in fish samples from Agbarho and Ekpan. There is no significant difference in mean of Hg for fish samples from all three locations at $p<0.05$. The highest levels of Cd was found in fish from Ogunu (0.02±0.00mg/kg) which is not statistically significant at $p<0.05$. The result is in line with that from the study conducted in cultured fish in Linggi estuary, Malaysia in which high concentration of Pb and Cd in the tissue of cultured fish were recorded (Shahrizat, 2005).

The concentration of heavy metals in crayfish samples shows that Ogunu had the highest levels of Zn (0.23±0.01mg/kg) and Cr (0.06±0.01mg/kg). The levels of Cu were below detectable limits in crayfish samples from all three locations. There is no significant difference in mean of Hg for fish samples from Agbarho (0.01±0.00^{a}mg/kg) and Ekpan (0.01±00.0^a mg/kg) locations at $p<0.05$. The highest levels of Pb was found in fish from Ogunu (0.04±0.02mg/kg) and Ekpan (0.04±0.02^{a}mg/kg) which is not statistically significant at $p<0.05$. Statistic ratio from the above findings suggest that predominant heavy metals like Cu and Cd as well as Pb can promote health issues that Cu and Cd as well as Pb are health threatening and continuous consumption of these aquatic food from polluted water body is unsafe.

The hazard quotient of cadmium in these seafoods samples showed that cadmium poses threat to the user of the water for both an adult and a child and the cancer risk for Cadmium fish were more than the limit of one person per a million persons (1 X10^{-6}). The application of phosphate fertilizers (Containing 2-200 mg Cd/kg), domestic and sewage sludge, wear of automobile tyres, lubricants and mining as well as metallurgical activities (metal smelting and refining) and fossil fuel burning were known source of cadmium that pollute aquatic environment (Fufeyin And Egborge, 1998; Sherene T. 2010). Cadmium is a dangerous metallic pollutant that is associated with chronic renal failure and skeletal damage with the concentration value in Fish sample showed that the concentration level of cadmium exceeds the average permissible limit value for Cadmium in the fish sample respectively. The transfer factor of cadmium was found to be above 1 (TF>1) for Tilapia and Catfish, which means that both fish species were bio-accumulating Cadmium. The mean maximum and minimum concentration value of cadmium during the dry season were 0.089 and 0.038 mg/kg and 0.027 and 0.004 mg/kg during the rainy season whereas, the mean concentration value of 0.05 ± 0.02 was obtained in a study conducted in 2012 around Ajaokuta steel company, a location that is about 25 km downstream of the confluence of rivers Niger and Benue. Long term exposure to cadmium could lead to carcinogenic occurrence in human kidney and lung damage, stomach irritation, vomiting as well as diarrhea (Olatunde *et al*., 2012).

Chromium and Copper showed hazard quotient (HQ), and transfer factor of less than 1 (HQ<1, TF<1) and indicates that they were both of less concern but, the chromium ions with concentration value more than the set limit could cause a deleterious effect on the long run. While Chromium concentration values in exceedance of set limit may increase the occurrence of goiter among humans and animals, copper, an essential micro-nutrient is required in the growth of both plants and animals. It helps in the production of blood hemoglobin in human and in plants, it helps in regulation of water and disease resistance but, in high dose, it can cause anemia, liver and kidney damage, stomach and intestinal irritation in animals. (Ekere *et al.*, 2014 Hait and Tare *et al*., 2012; Lenntech, 2009; WHO,2010).

Zinc concentration values in fish were higher than the set limit and therefore showed transfer factor that were greater than 1 (TF>1). Zinc occurs naturally in air, water and soil, but zinc concentrations may have unusually arisen, due to addition of zinc through human activities. Mostly zinc are been added to the environment during industrial activities such as coal mining and waste combustion and steel processing. Many foodstuffs contain certain concentration of zinc Fish can accumulate and bio-magnify zinc in the food chain (WHO, 2010) as observed.

Lead (Pb) arises in the environment from both natural and anthropogenic source. Exposure can be through drinking water, food, air, soil and even dust from old paint containing lead. Lead is used in the manufacturing, construction and chemical industries. It is used in batteries, alloys, pigments, cable sheathing and in guns and ammunition. Exposure to lead in humans can result in a wide range of biological effects depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn causes problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tracts, joints and reproductive systems and acute or chronic damage to the nervous system (Hait and Tare *et al*., 2012).

5.2 Polycyclic Aromatic Hydrocarbon

Organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), are also a major reason for deformity and cancer. The presence of some PAHs has shown increased incidence of skin, lung, and bladder, liver, and stomach cancers in laboratory animals (Armstrong *et al*., 2004; Boffetta *et al*., 1997; Bosetti *et al*., 2007; Kogevinas *et al*., 2003).

The result obtained from the determination of the PAHs contents of the crab samples as presented in (Table 4.10) indicates that there was the presence of LMW pahs such as Fluorene (0.001 mg/kg), Naphthalene (0.001 mg/kg) and phenanthrene (0.009 mg/kg) in crab samples from Agbarho while there was the absence of Acenaphthene and Acenaphthylene. Phenanthrene was found in crabs from all three communities which indicates it persistence. The subtotal of LMW indicates the following order, Ogunu (0.033 mg/kg)> Ekpan (0.013 mg/kg)>Agbarho (0.011 mg/kg). The medium molecular weight pahs studies found Flouranthene was present in crab samples from Ekpan (0.001 mg/kg) and Ogunu (0.001 mg/kg) whereas it was absent in samples from Agbarho. Pyrene was absent in Ogunu but present in Agbarho (0.003 mg/kg) and Ekpan (0.001 mg/kg). The subtotal MMW mean indicates that the following order Agbarho (0.003 mg/kg)> Ekpan (0.002 mg/kg)>Ogunu (0.001 mg/kg). The result of HMW indicates the presence of ά Dibenzyl(g-h)anthralene (0.002 mg/kg), Benzo (g) pyrence (0.017 mg/kg), Benzo (g-h-i) perylene (0.001 mg/kg), Benzo(b) fluoranthene (0.006 mg/kg) in crab sample from Ogunu. The pah, 1,2-benzanthracene was found absent in crabs samples from Ekpan and Ogunu. The subtotal of HMW was found higher in crab samples from Ogunu (0.01 mg/kg) when compared to Agbarho (0.008 mg/kg) and Ekpan (0.007 mg/kg) at $p<0.05$. The sum total of PAHs contents were found higher in crab samples from Ogunu (0.012 mg/kg) with no difference in mean for Agbarho (0.022 mg/kg) and Ekpan (0.022 mg/kg). This outcome indicate Crab from this body of water are not safe for human consumption, therefore must be avoided.

The result obtained from the determination of the PAHs contents of the fish samples as presented in (Table 4.11) revealed that there was the presence of LMW PAHs such as Fluorene (0.003 mg/kg), Naphthalene (0.001 mg/kg) and Acenaphthene (0.009 mg/kg) in fish samples from Ekpan while there was the absence of Phenanthrene and Acenaphthylene. Agbarhohad only Phenanthrene (0.003 mg/kg), and Naphthalene (0.001 mg/kg) while fish samples from Ogunu had Phenanthrene (0.013 mg/kg) and Acenaphthylene (0.001 mg/kg). The subtotal of LMW indicates the following order, Ogunu (0.014 mg/kg)> Ekpan (0.005 mg/kg)>Agbarho (0.004 mg/kg). The medium molecular weight PAHs (Flouranthene and Pyrene) studies shows that Flouranthene was present in fish samples from Agbarho and Ekpan had the same mean concentration of 0.001 mg/kg and Ogunu (0.001 mg/kg) whereas it was absent in samples from Ogunu. Pyrene was absent in Ogunu but present in Ekpan (0.001 mg/kg). The subtotal MMW mean indicates that the following order Ekpan (0.002 mg/kg)>Agbarho (0.001 mg/kg)>Ogunu (0.000 mg/kg). High molecular weight PAHs result indicates the presence of Dibenzyl(g-h)anthralene (0.002 mg/kg), Benzo (g) pyrence (0.015 mg/kg), Benzo (g-h-i) perylene (0.001 mg/kg), Benzo(b) fluoranthene (0.004 mg/kg) and xylene (0.001 mg/kg) in fish sample from Ogunu. The pah, 1,2-benzanthracene was found absent in fish samples from Ekpan and Ogunu. The subtotal of HMW was found higher in fish samples from Ogunu (0.023 mg/kg) when compared to Agbarho (0.00 mg/kg) and Ekpan (0.01 mg/kg) at $p<0.05$. The sum total of PAHs contents were found higher in fish samples from Ogunu (0.0224 mg/kg)> Ekpan (0.017 mg/kg) >Agbarho (0.014 mg/kg). These out come all in line with a study conducted by(CEPA, 1994)The increased level of PAHs in the sample is consistent with the studies of Duke and Albert (2007) who found varying concentrations of PAHs in samples from Delta State, Nigeria. There was high amount of PAHs in river water experiment carried out by (cheng *et al.*, 2002) showed the rate of toxicity in fish from a stream used by all in his village. From all clearly indication consumption of fishes from such rivers can lead serious damage to vital organs in the body. Benzo[a]pyrene concentration values in water and Catfish stands high comparing with the concentration limit of 0.01 µg/L in water by Environment Canada and been a common marker for PAHs originating from combustion, it presence above the set limit indicates that threat of PAHs exist for the rivers location.

The result obtained from the determination of the PAHs contents of the crayfish samples as presented in Table indicates that there was the presence of LMW PAHs such as Fluorene (0.002 mg/kg), Naphthalene (0.001 mg/kg) and Phenanthrene (0.009 mg/kg) in crayfish samples from Agbarho while there was the absence of Acenaphthene, Anthracene and Acenaphthylene. Phenanthrene was found present in all three crayfish samples. Crayfish samples from Ekpan had Acenaphthene (0.006 kg/mg), Fluorene 0.005 mg/kg), and Phenanthrene (0.001 mg/kg). The subtotal of LMW indicates that Ogunu had the highest LMW PAHs (0.732 mg/kg) while no significant difference was observed in the mean of Agbarho (0.012 kg/mg) and Ekpan (0.012 kg/mg) at $p<0.05$. The medium molecular weight studies shows that Flouranthene was present in crayfish samples from Ekpan (0.001 mg/kg) but fall below detectable limit in crayfish samples from Agbarho and Ogunu. Pyrene was present in Ekpan but absent in Ogunu. The subtotal mean levels were higher in Ekpan (0.002 mg/kg) and Ogunu (0.001 mg/kg). High molecular weight (HMW) studies indicates the presence of Benzo (g) pyrence (0.005 mg/kg), Benzo (g-h-i) perylene (0.001 mg/kg), 1,2-benzanthracene (0.001 mg/kg) in crayfish sample from Agbarho while Dibenzyl(gh)anthralene, Benzo (k)fluoranthene and Xylene were absent. The subtotal of HMW was found higher in crayfish samples from Ogunu (0.021 mg/kg) when compared to Agbarho (0.007 mg/kg) and Ekpan (0.006 mg/kg) at $p<0.05$. The sum total of PAHs contents were found higher in crayfish samples from Ogunu (0.762 mg/kg)> Ekpan (0.02 mg/kg) >Agbarho (0.01 mg/kg).From clear indication the crayfish from the study all contain PAHs though in vary quantity, Feeding on crayfish from these water body could be very risky as accumulations could lead to toxicity. This findings is in strong agreement with that of (Eisler, 1987).

6. CONCLUSION

From the foregoing discussion it can be concluded the level of heavy metals and PAHs were high in samples from Ogunu and Ekpan. The high level of heavy metals and PAHs in seafood samples in these crude oil impacted communities is obviously a cause for concern as these contaminants may make seafood (a major source of protein and vital nutrient) unhealthy for human, livestock and industrial uses especially for people within the coastal area. It is recommended that the residents within or nearby the communities should be educated on dangers involved in the consumption of foods from Ogunu and Ekpan rivers. This is because if not checked, continuous accumulation of these pollutants may expose people to whole lot of health complications. This also calls for need for routine analysis of seafood samples that are to be transported to other parts of the country before it can be satisfied safe for consumption.

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