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Heavy Metals and Hydrocarbon Level in Nile Tilapia (*Oreochromis niloticus),* Mullet Fish (*Liza falcipinus*) and Crab (*Callinectes amnicola)* from Crude Oil Contaminated Jetty Rivers in Port Harcourt, Nigeria

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ABSTRACT: In this study, the level of polycyclic aromatic hydrocarbons and heavy metals (Pb, Cr, Zn, Cd, Cu, Fe and Mn) contamination were determined in Nile tilapia, Mullet fish and Crab collected from crude oil polluted rivers (Abuloma and Woji Jetty). Average individual PAHs concentration ranged from 0.0001mgkg^{-1} to 11.22±0.02mgkg^{-1} in Nile tilapia, 0.0001mgkg^{-1} to 13.43±0.17mgkg^{-1} in mullet fish and 0.0001mgkg^{-1} to 12.23±0.06mgkg^{-1} in crab. Benzo[a]pyrene (a carcinogenic PAH) concentrations detected in fish and seafood in this study exceeded the acceptable limit set by the European Commission (0.002mgkg^{-1}) for fish considered safe for human consumption. The levels of Pb and Cr in fish and seafood were found to have remarkably higher concentrations which exceeded the acceptable levels (FAO/WHO) in food sources for human consumptionand that of Cd, Fe, Zn, Cu and Mn were lower. Results from this study revealed high levels of PAHs and heavy metals in seafood samples from all study locations. These high PAHs levels in these commonly consumed seafoods from the rivers question their safety for human consumption.

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Crude oil has been vital in financing the nation's economic growth and development but pollution is generally believed to be the necessary price for the development ushered in by the petroleum industry. It has been asserted that even in the best oil field practice, oil spillage cannot be completely eliminated (Ekpu, 1996; Aghalino, 1999). Crude oil is refined into fuels, including petrol, kerosene, jet fuel, diesel fuel, furnace oil etc. It is also the source of greases and waxes. When these products are being refined and transported, oil spillages may occur resulting to the introduction of harmful chemicals like heavy metals, polycyclic aromatic hydrocarbons and so on into the environment that can result into contamination of the air, soil and water bodies. Polycyclic aromatic hydrocarbons are found in crude oil andpetroleum based fuels; therefore they can be emitted to the environment during spills of petroleum containing products (Aislabie *et al.*, 1999). PAHs are emitted and found in the environment as a mixture of pollutants from thisgroup.Compared to other types of water pollutants, heavy metals pollution is less visible, but their effects on the ecosystem and human beings can be intensive and very extensive. Thus, it has become a great concern in recent years because they are very harmful due to their non-biodegradable nature, long biological half-life and their potential to accumulate in different body parts of organism. They can be also concentrated along the food chain, producing their toxic effect at points after far removed from the source of pollution.Many heavy metals are carcinogenic, immunogenic, or mutagenic (USEPA, 1993). Aquatic

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organisms as well as plants provides majority of the proteins present in food taken by humans. Seafood is a remarkably low-caloric food containing a high amount of protein that supports effective health condition (Ayotunde *et al.,* 2012). Fish are important bioindicator species and play an important role in the monitoring of water pollutionbecause they respond with great sensitivity to changes in the aquatic environment (Naigaga *et al.,* 2011).Seafood naturally contains vitamins and minerals such as B-complex vitamins, vitamin D and vitamin B. These vitamins carry out several functions like improving energy production, metabolism, concentration, and also body beauty (Madison, 2007). Continual exposure of marine species to PAHs can result to developmental complications, vulnerability to diseases and unusual reproductive cycles (Panetta, 2003). Heavy metals contamination of foods (including aquatic species) can be very serious considering the health implications of consumption of high levels of heavy metals or continuous consumption of small amounts over a period of time (Galadima and Garba, 2012). Therefore detection of pollutants in these species can be of risk to the health of the public (Cirillo *et al.*, 2009).

MATERIALS AND METHODS

Study area: Abuloma and Woji Jetty located in Port Harcourt and Obio Akpor local government area of Rivers state were selected for this study. Abuloma and Woji Jetty is characterized by heavy industrialactivities (such as loading and transportation of petroleum products, wood, sand and gravel; construction and maintenance of marine vessels, tugboats and barges) which may impact the coastalenvironment. In addition, shipping activitiesat the jetty may impact the coastalenvironment through accidentaloil leakage and spillage,most especially during the discharge of crude oil products atthe shoreline of the river. Inhabitants of these communities engage majorly in fishing and farming. The Abuloma and Woji rivers are also linked to other communities like Okujagu-ama, Azuabie town, Okuru-ama, Oginigba and Kalio-ama, which makes it economically relevant for industries to flourish on daily basis. Ojimba-ama located in Okrika local government area of Rivers State served as the control site for this study. The Ojimba-ama River served as control for this study because most of the industrial activities carried out on Abuloma and Woji Jetty Rivers are not found here.

Sample collection, preparation and analysis: Fresh samples of *Oreochromis niloticus* (Nile Tilapia)*, Liza falcipinus* (Mullet fish) and *Callinectesamnicola* (Crab) were collected from Abuloma Jetty, Woji Jetty and Ojimba-ama (Control) river. Frozen ice chest was used to convey the samples from the three sites to the laboratory where three individual fishes and crabs of same sizes were collected, cleansed, covered and packed in aluminium foils. At the laboratory, the samples were placed in an air drying oven for about 18hours at 70^0C and then ground with a corona grinder (Manual grinding machine). The ground samples were allowed to undergo extraction and analyzed for PAHs.Two grams (2g) of sample was measured into a clean extraction container and about 10ml of the extraction solvent (DCM) was introduced into the sample where complete mixing was done and allowed to settle. A filter paper fitted into Buchner funnels was used to carefully filter the samples into a clean solvent-rinsed extraction bottle. The extract obtained was concentrated to 2ml and removed for cleaning.

Analysis of PAHs was done using an Agilent 6890N gas chromatograph with flame ionization detector (GC/FID), equipped with an injector fused with a silica capillary column (DB-5ms). Heavy metals (Pb, Cr, Zn, Cd, Cu, Fe and Mn) concentrations were determined using atomic absorption spectrophotometer (AAS). Triplicate analyses were performed for all the samples.

Statistical Analysis: Data obtained were subjected to Analysis of variance (ANOVA) using the statistical package SPSS (version 21) and test of significance was done at 95 % confidence level.

RESULTS AND DISCUSSION

Polycyclic Aromatic Hydrocarbons (PAHs) concentrations in studied Nile tilapia, Mullet and Crab Samples: Table 1 shows the mean concentrations of individual PAHs and total mean PAHs concentrations in Nile tilapia samples from Abuloma, Woji and Ojimba-ama Rivers. In Nile tilapia from Abuloma, Woji and Ojimba-ama Rivers, 16 PAHs were analyzed in which average concentrations of PAHs ranged from detection limits of 0.0001mgkg^{-1} to 11.22±0.02mgkg^{-1} where a total of 7, 5 and 3 PAHs were detected in the Tilapia samples from Abuloma, Woji and Ojimba-ama Rivers respectively. The total concentration of PAHs in Tilapia samples from Abuloma, Woji and Ojimba-ama Rivers were 29.84±0.72mgkg^{-1}, 16.36±0.67mgkg^{-1} and 11.58±0.16mgkg^{-1} respectively. Total PAHs in Tilapia samples from the three sites varied significantly ($p<0.05$) across each other with Woji having the highest value followed by Abuloma then Ojimba-ama which may be as a result of the high contaminating activities at the Woji and Abuloma Jetty compared to the less contaminating activities at Ojimba-ama. This study showed a high presence of Pyrene, Acenaphtene and Phenanthrene in Nile Tilapia across the three locations. There was no significant difference ($p<0.05$) in fluorine, fluoranthene, Benz(a)anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benz(a)pyrene, indeno[1,2,3-cd]pyrene, Benzo[g,h,i]perylene and dibenz[a,h]anthracene concentrations of Tilapia samplesacross all the sites.

Mean concentrations of individual PAHs and total mean PAHs concentrations in Mullet fish samples from Abuloma, Woji and Ojimba-ama Rivers were shown in Table 2. In Mullet fish from Abuloma, Woji and Ojimba-ama Rivers, 16 PAHs were analyzed in which average concentrations of PAHs ranged from detection limits of $0.0001mgkg^{-1}$ to $13.43±0.17mgkg^{-1}$ where a total of 9, 8 and 6 PAHs were detected in the Mullet fish samples from Abuloma, Woji and Ojimba-ama Rivers respectively. The total concentration of PAHs in Mullet fish samples from Abuloma, Woji and Ojimba-ama Rivers were $42.62±1.39mgkg^{-1}$, $30.01±0.88mgkg^{-1}$ and $25.80±0.38mgkg^{-1}$ respectively. Total PAHs in Mullet samples from the three sites varied significantly ($p<0.05$) across each other with Abuloma having the highest value followed by Woji then Ojimba-ama. This can be due to high presence of contaminates from accidental oil spillage, indiscriminate dumping of refuse, industrial activities and other daily activities carried out on the river which has led to the bioaccumulation of harmful pollutants in the Mullet fish. In this study, individual PAHs such as Pyrene, Acenaphtene, FlouranthenePhenanthrene, Chrysene, Naphthalene and Acenaphtalene bioaccumulation were seen in Mullet fish across the three locations. There was no significant difference ($p<0.05$) in acenaphthene, fluorine, Benz(a)anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, Benzo[g,h,i]perylene and dibenz[a,h]anthracene concentrations of Mullet samples across all the three locations.

Table 1: Polycyclic Aromatic Hydrocarbon (PAHs) concentrations in studied Nile tilapia (*Oreochromis niloticus)* samples

PAHs ($mgkg^{-1}$)	Abuloma Jetty	Woji Jetty	Ojimba Ama
Naphthalene	$2.14±0.09^a$	BDL^b	BDL^b
Acenaphthylene	$5.52±0.12^a$	$1.54±0.59^b$	BDL^c
Acenaphthene	$1.44±0.09^a$	$4.09±0.03^b$	$3.29±0.12^c$
Fluorene	BDL	BDL	BDL
Anthracene	$3.34±0.16^a$	$1.16±0.01^b$	BDL^a
Phenanthrene	$11.22±0.02^a$	$2.55±0.04^b$	$2.12±0.03^a$
Fluoranthene	BDL	BDL	BDL
Pyrene	$4.54±0.09^a$	$7.02±0.01^b$	$6.17±0.01^c$
Benz[a]anthracene	BDL	BDL	BDL
Chrysene	$1.64±0.15^a$	BDL^a	BDL^a
Benzo[b]Fluoranthene	BDL	BDL	BDL
Benzo[k]Fluoranthene	BDL	BDL	BDL
Benzo[a]pyrene	BDL	BDL	BDL
Indeno[1,2,3-cd]Pyrene	BDL	BDL	BDL
Benzo[g, h, i]perylene	BDL	BDL	BDL
Dibenz[a, h]anthracene	BDL	BDL	BDL
Total PAHs	$29.84±0.72^a$	$16.36±0.67^b$	$11.58±0.16^c$

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row aresignificantly different while values with same superscript within a row are not significantly different ($p<0.05$).
BDL= below detection limits of $0.0001mgkg^{-1}$

Mean concentrations of individual PAHs and total mean PAHs concentrations in Crab samples from Abuloma, Woji and Ojimba-ama Rivers were shown in Table 3. In Crab samples from Abuloma, Woji and Ojimba-ama Rivers, 16 PAHs were analyzed in which average concentrations of PAHs ranged from below detection limits of $0.0001mgkg^{-1}$ to $12.23±0.06mgkg^{-1}$ where a total of 7, 8 and 6 PAHs were detected in the Crab samples from Abuloma, Woji and Ojimba-ama Rivers respectively. The total concentration of PAHs in Crab samples from Abuloma, Woji and Ojimba-ama Rivers were $39.32±0.97mgkg^{-1}$, $27.42±0.05mgkg^{-1}$ and $21.37±0.67mgkg^{-1}$ respectively and they all varied significantly ($p<0.05$) across locations with Abuloma having the highest value followed by Woji then Ojimba-ama which may be as a result of the high contaminating activities at the Woji and Abuloma Jetty compared to the activities at Ojimba-ama river. There was no significant difference ($p<0.05$) in fluorine, fluoranthene, Benz(a)anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benz(a)pyrene, indeno[1,2,3-cd]pyrene, Benzo[g,h,i]perylene and dibenz[a,h]anthracene concentrations of Crab samplesfrom all the three locations. Exposure pathways of polycyclic aromatic hydrocarbons (PAHs) to fish include bioconcentration from water across their gills and skin (Gobas *et. al*., 1999) and ingestion of PAH-contaminated particulate matter along with food (Meador *et al.*, 1995), as PAHs readily adsorb onto particulate organic matter (Fowler and Knauer, 1986) especially soil sediments. One of the predominant exposure routes of PAH is through diets; fishes serve as a major diet for humans. As chemically stable and lipophilic compounds (Bouloubassi *et al.*, 2006), PAH can easily cross lipid membrane and have the potential to bioaccumulate in aquatic organisms. Pyrene and Chrysene were the most abundant carcinogenic PAHs present in majority of the samples across all the sites in this study. The results further showed that in all the samples analyzed, Mullet samples from Abuloma contained the highest amount of total PAHs with predominance of carcinogenic PAHs. The observed differences in PAH bioaccumulation in both species may also be attributed to differences in feeding preferences and general behavior (Fisher, 1995), as well as the mode of feeding in these species (Kong *et al.*, 2005). These high PAHs concentrations in the aquatic organisms could be as a result of pollutants from combustion of petroleum products, refuse dump, abattoir, waste water, sewage discharge, dredging and other industrial activities performed on the river. It would be observed that value of Benzo[a]pyrene concentrations across all the samples exceeded the European Union (EU) limit of 2 µg/kg wet wt. for fish, the safe level for human consumption. Although, European Union (EU) limit of 5µg g^{-1} wet wt (EU, 2006) for Indeno[1,2,3-cd]pyrene was not exceeded in all the samples. Nevertheless, fish species could be an important source of PAHs exposure among people living in Abuloma, Woji and Ojimba-ama.

Table 2: Polycyclic Aromatic Hydrocarbon (PAHs) concentrations in studied Mullet fish (*Liza falcipinus*) samples

PAHs ($mgkg^{-1}$)	Abuloma Jetty	Woji Jetty	Ojimba-Ama
Naphthalene	2.22±0.18 [a]	3.18±0.11[b]	2.25±0.12[c]
Acenaphthylene	13.43±0.17[a]	8.44±0.09[b]	7.12±0.05[c]
Acenaphthene	1.38±0.28 [a]	BDL [b]	BDL [b]
Fluorene	BDL	BDL	BDL
Anthracene	3.36±0.13[a]	1.38±0.18[b]	BDL [c]
Phenanthrene	2.31±0.21[a]	4.46±0.23[b]	9.58±0.08[c]
Fluoranthene	BDL [a]	3.28±0.05[b]	1.21±0.01[c]
Pyrene	10.46±0.08[a]	5.30±0.03[b]	2.14±0.07[c]
Benz[a]anthracene	BDL	BDL	BDL
Chrysene	4.64±0.11[a]	2.62±0.10[b]	3.50±0.05[c]
Benzo[b]Fluoranthene	1.46±0.08 [a]	BDL[b]	BDL[b]
Benzo[k]Fluoranthene	BDL	BDL	BDL
Benzo[a]pyrene	3.36±0.15[a]	1.35±0.09[b]	BDL [c]
Indeno[1,2,3-cd]Pyrene	BDL	BDL	BDL
Benzo[g, h, i]perylene	BDL	BDL	BDL
Dibenz[a, h]anthracene	BDL	BDL	BDL
Total PAHs	42.62±1.39 [a]	30.01±0.88[b]	25.80±0.38[c]

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row aresignificantly different while values with same superscript within a row are not significantly different (p<0.05).
BDL= below detection limits of 0.0001$mgkg^{-1}$

Table 3: Polycyclic Aromatic Hydrocarbon (PAHs) concentrations in studied Crab (*Callinectes amnicola)* samples

PAHs ($mgkg^{-1}$)	Abuloma Jetty	Woji Jetty	Ojimba-Ama
Naphthalene	1.29±0.12[a]	2.42±0.05[b]	1.56±0.08[c]
Acenaphthylene	7.27±0.13[a]	3.08±0.04[b]	BDL [c]
Acenaphthene	3.37±0.18[a]	1.20±0.03[b]	1.41±0.21[c]
Fluorene	BDL	BDL	BDL
Anthracene	4.49±0.16[a]	2.80±0.01[b]	2.39±0.16[c]
Phenanthrene	9.27±0.19[a]	6.17±0.02[b]	5.54±0.10[c]
Fluoranthene	BDL [a]	1.36±0.03[b]	BDL [c]
Pyrene	12.23±0.06[a]	9.22±0.05[b]	7.08±0.02[c]
Benz[a]anthracene	BDL	BDL	BDL
Chrysene	1.40±0.13 [a]	1.17±0.02[b]	3.39±0.10[c]
Benzo[b]Fluoranthene	BDL	BDL	BDL
Benzo[k]Fluoranthene	BDL	BDL	BDL
Benzo[a]pyrene	BDL	BDL	BDL
Indeno[1,2,3-cd]Pyrene	BDL	BDL	BDL
Benzo[g, h, i]perylene	BDL	BDL	BDL
Dibenz[a, h]anthracene	BDL	BDL	BDL
Total PAHs	39.32±0.97[a]	27.42±0.05[b]	21.37±0.67[c]

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row aresignificantly different while values with same superscript within a row are not significantly different (p<0.05).
BDL= below detection limits of 0.0001$mgkg^{-1}$

PAHs concentration in Tilapia, Mullet and Crab samples in this study were lower than the amount of 70.440µgg^{-1}wet wt. which was obtained among five species of fish samples collected along the harbor line, Mumbai (Dhananjayan *et al.*, 2012) and greater than 3.365ppm obtained in edible fishes of the Gomtiriver, Lucknow, India (Malik *et al.*, 2008). The values of PAHs concentration were within the range reported by Nwaichi and Ntorgbo (2016) which showed that PAHs concentration in fish and seafoods from 3 coastal rivers in Niger Delta region (Sime, Kporghor and Iko) ranged from 3.670±0.050$\mu g g^{-1}$ - 171.900±0.450 $\mu g g^{-1}$. Consumers of aquatic organisms around these areas that depends on fish and seafood from these rivers should be particularly cautious of the excessive amount of carcinogenic PAHs in the samples, having recorded the very high amount of carcinogenic PAHs, and as such, are capable of producing significant health threats like growth reduction (Christiansen and George, 1995), endocrine alteration (Meador *et al.*, 2006), malformations of embryo and larvae (Carls *et al*., 2008; Camus and Olsen, 2008) and DNA damage (Caliani *et al*., 2009) in fish, as well as human health effects such as cancer, mutations and birth defects (Zedec, 1980; White, 1986), they may also have adverse impacts on marine life (Nyarko *et. al.,* 2011)

Heavy metal concentrations in studied Nile tilapia, Mullet fish and Crab samples: In aquaticecosystems, fishes are considered as good representativeindicators of the overall system of health, due to theirrelatively higher position occupied in the food-chain (Adams *et al.,* 1993). Marine organisms, including fish, accumulate heavymetals through direct absorption, or via food chain, and pass them to human beings by consumption, causing acute chronic or disorders (Eastmond *et al.*, 2008).It is worth to mention that the essential metals, such as iron, zinc, copper and manganese are in higher concentrations, presumably due to their function as co-factors for the activation of a number of enzymes and regulated to maintain a certain homeostatic status in fish. On the other hand, the non-essential metals such as cadmium and lead has no biological function or requirement and its concentrations in fishes are generally low (Kumar *et al*., 2011). The results of this study showed that lead (Pb) was present in all the fish and crab samples and were accumulated in high concentrations for some samples which were higher than the recommended limit of FAO/WHO (2.0ppm).This implies that these aquatic organisms are contaminated with Pb.

The high lead content may beattributed to a higher state of contamination from the use of leaded gasoline (GESAMP, 1991) during operation in and around the river and also other industrial activities. Lead most likely interferes with functions performed by essential mineral such as calcium, iron, copper, andzinc, especially several red blood cell enzyme systems. Lead causes toxicity by replacing zinc in heme synthesis and inhibiting the function of heme-synthesizing enzymes (Goyer and Clarkson, 2001). Several studies have reported higher levels of Pb in different fish samples from some Nigerian rivers.The values obtained for lead in this study are higher than that of Daka *et al.*, (2008) who obtained 0.01-0.06ppm in fish species from Azuabie Creek in the Bonny Estuary, Nigeria. Some results obtained in this study fell in line with Doherty *et al*. (2010) that reported 0.44ppm and 0.62ppm of lead in *C. nigrodigitatus* and *T.guineensis* respectively.

Table 4: Heavy metal concentrations in studied Nile Tilapia (*Oreochromis niloticus)* samples

Heavy Metal (ppm)	Abuloma Jetty	Woji Jetty	Ojimba-Ama	FAO/WHO Standard (2003)
Pb	0.83±0.01^{a}	1.36±0.00^{b}	0.50±0.01^{c}	2
Cd	0.02±0.00^{a}	0.01±0.00^{a}	BDL^{a}	2.0
Cr	3.14±0.03^{a}	1.00±0.00^{b}	1.37±0.01^{c}	0.15
Fe	4.64±0.01^{a}	3.96±0.02^{b}	4.11±0.01^{c}	100
Zn	2.52±0.02^{a}	3.23±0.04^{b}	3.17±0.00^{c}	75
Cu	0.17±0.00^{a}	0.05±0.00^{b}	0.09±0.00^{a}	30
Mn	0.51±0.01^{a}	0.19±0.00^{a}	0.40±0.00^{a}	5.5

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row aresignificantly different while values with same superscript within a row are not significantly different ($p<0.05$).

Table 5: Heavy metal concentrations in studied Mullet fish (*Liza falcipinus*) samples

Heavy Metal (ppm)	Abuloma Jetty	Woji Jetty	Ojimba-Ama	FAO/WHO Standard (2003)
Pb	1.53±0.08^{a}	3.00±0.00^{b}	0.59±0.01^{c}	2
Cd	0.07±0.00^{a}	0.02±0.00^{a}	0.08±0.00^{a}	2.0
Cr	5.30±0.00^{a}	1.80±0.00^{b}	2.12±0.01^{c}	0.15
Fe	2.76±0.03^{a}	1.40±0.00^{b}	1.97±0.03^{c}	100
Zn	3.45±0.04^{a}	3.02±0.04^{b}	3.35±0.09^{c}	75
Cu	0.93±0.01^{a}	0.74±0.01^{b}	0.62±0.00^{c}	30
Mn	0.86±0.01^{a}	0.59±0.01^{b}	0.22±0.00^{c}	5.5

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row aresignificantly different while values with same superscript within a row are not significantly different ($p<0.05$).

Cadmium was also detected in all the samples except Tilapia fish from Ojimba-ama but the highest concentration of Cd was observed in crab samples obtained from Abuloma River (0.38±0.00ppm). All the concentrations of cadmium fell below the FAO/WHO permissible limit of 2.0ppm. This indicates a very low presence of Cd in the samples. These low levels may increase in future if not properly checked. This may be as a due to presence of pollutants from industrial activities and transportation of petroleum products at the shoreline of the rivers. Järup, 2003 reported that Osteomalacia and kidney damage can be caused by frequent bioaccumulation of Cd. Saha*et al.,* (2013) documented that Cd is known as an endocrine disturbing substance and can lead to the development of breast cancer and prostate cancer in humans. Cd also causes damage in kidney, hypertension, tumours, poor reproductive performance and hepatic dysfunction (Al-Busaidi *et al.,* 2011; Rahman and Islam 2010). Chromium is an essential trace element and plays animportant role in fish metabolism (Sthanadar *et al.,* 2013). The results of this study also showed that Chromium (Cr) was detected in all the fish and crab samples in high quantities. Crab samples from Abuloma River had the highest concentration of Cr(6.72±0.11ppm) and the concentration of Cu obtained across all the fish and crab samples wasgenerally higher than the FAO/WHO standard (0.15ppm). This indicates a Cu pollution of these samples which could be attributed to the discharges from the industries operating on the river and refuse discharges. Rauf *et al*. (2009) have recorded a high level of Chromium in fish species, *Catlacatla*, *Labeorohita* and *Cirrhinamrigala* caught from the River Raviin Pakistan. USFDA, (1993) has explained that in vitro studies indicated that high concentrationsof chromium (III) in the cell can lead to DNA damage. Also, Chromium reaches the blood stream; itdamages the kidneys, the liver, and blood cells through oxidation reactions.

Table 6: Heavy metal concentrations in studied Crab (*Callinectes amnicola)* samples

Heavy Metal (ppm)	Abuloma Jetty	Woji Jetty	Ojimba-Ama	FAO/WHO Standard (2003)
Pb	2.88±0.02[a]	5.01±0.01[b]	1.31±0.02[c]	2
Cd	0.38±0.00[a]	0.08±0.00[a]	0.04±0.00[a]	2.0
Cr	6.72±0.11[a]	3.02±0.06[b]	3.71±0.08[c]	0.15
Fe	7.17±0.04[a]	5.29±0.01[b]	7.31±0.01[c]	100
Zn	4.93±0.03[a]	5.60±0.05[b]	4.25±0.02[c]	75
Cu	2.73±0.01[a]	3.01±0.00[b]	2.26±0.04[c]	30
Mn	2.98±0.02[a]	3.39±0.10[b]	2.31±0.02[c]	5.5

Values are expressed as means ± standard error of mean (SEM) of three replicates. Values with different superscript in the same row aresignificantly different while values with the same superscript within a row are not significantly different (p<0.05).

The results of this study showed that Iron (Fe) was detected in all the fish and crab samples but were accumulated in concentrations that fell within the permissible limit of FAO/WHO (100.0ppm). This indicates that Fe concentrations in these aquatic organisms may not pose serious health consequences to consumers at short term of exposure but could be in the long run. Crab samples from Ojimba-ama River recorded the highest level of Zn (7.31±0.01ppm). This difference noticed in the levels of accumulation in different heavy metals in the organisms can be attributed to the differences in their physiological roles toward maintaining homeostasis, feeding habits, regulatory ability and behavior of each fish. This is a justification of the report of Cross *et al.* (1973) which explain that metal accumulation could be related to fish feeding habits. Iron (Fe) is a mineral essential for every living cell and necessary for the synthesis of myoglobin, haemoglobin and certain enzymes. Anaemia disease gives poor performance in circulatory transport and also reduces oxygen supply to muscle, less efficiency due to the decreasing of myoglobin content and impairing endurance capacity (Erdman *et al.,* 2012). Zinc was also detected in all the samples and recorded the highest concentration in crab samples obtained from Woji River (5.60±0.05ppm). The levels of Zn bioaccumulation in all the samples were below the maximum limit of FAO/WHO (75.0ppm). This shows that the aquatic organisms present in the three locations are not at risk of zinc toxicity. Zn is known as a cofactor to more than 300 enzymes that involved in RNA and DNA metabolism (Chasapis *et al.,* 2012).When exceeding amounts are present, Zn becomes toxic but a deficiency of Zn can lead to several disorders such as results in poor pregnancy outcomes and development of chronic diseases, including cardiovascular disease and also cause cancer (Kasi *et al.,* 2010). Copper was detected in all the fish and crab samples, and were accumulated in low concentrations that fell within the permissible limit of FAO/WHO (30.0ppm). Copper (Cu) is an essential metal of enzymes and necessary for the haemoglobin synthesis (Sivaperumal *et al.,* 2007). Impaired delivery of Cu can result in decreased cuproenzyme activity, the skeletal and vascular systems and also cause anaemia, neutropenia and osteoporosis (Angelova *et al.,* 2011). Excessive intake of Cu also could cause kidney damage and even death (ATSDR, 1999).

Manganese is an element of low toxicity that has considerable biological significance due their ability to prevent heart attack, stroke and cardiac arrest.The results of this study showed that Manganese (Mn) was detected in all the fish and crab samples and these levels were lower than the permissible limit of FAO/WHO (5.5ppm). This indicates a low presence of Mn in the samples. This low level may increase in future if not properly checked. Crab samples from Woji River recorded the highest level of Mn (3.39±0.10ppm). This increased level of Mn in Crab samples of Abuloma and Woji may be attributed to the welding works, industrial activities and refuse disposal on the River. Deficiency of Mn gave congenital malformations in offspring, poor growth performance and low efficiency of the reproductive system (Goldhaber, 2003). However, it’s become dangerous and toxic at high concentrations and usually may lead to the neurologic and psychological disorder (Saha and Saman, 2013).

Conclusion: This study determined the level of polycyclic aromatic hydrocarbons and heavy metal concentration in Nile tilapia, Mullet fish and Crab from crude oil contaminated rivers in Abuloma Jetty, Woji Jetty and Ojimba-ama. The results showed that the accumulation of heavy metals and PAHs in seafood exceeded the maximum permissible limits. Therefore, studied species indicated high level of PAHs and heavy metal contamination which can lead to exposure of the population that feeds on these aquatic organisms to several health challenges.

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