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Comparative Assessment of Polycyclic Aromatic Hydrocarbons (PAHS) and Heavy Metals in Catfish from Rivers, Swamp and Commercial Fish Ponds in Oil and Non-Oil Polluted Areas in Rivers And Anambra States.

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Abstract: *This study comparatively assessed the bioaccumulation of some PAHs and heavy metals by catfish harvested from rivers, swamp and commercial fish ponds in oil polluted and non-oil polluted areas. Three fishes were collected from each of the following sites; Akaraolu swamps in Ahoada East LGA (AR), a commercial fish pond within the area (AP), The New Calabar River in Ikwerre LGA (BR), a fish pond within the area (BP), Omambala River, Anambra East LGA (CR), a fish pond in Awka, Anambra state (CP), six groups in all. All analyses were done following standard procedures. Following analysis, there was no significant difference in the PAHs concentration for all sites. The Ni Pb, and Cr values were greater than the WHO limits (0.5, 0.4 and 1.0mg/kg respectively), their concentrations were in this order; CR>BR>AR (Ni and Cr), CR>AR>BR (Pb), and was the same for the ponds. Zn concentrations ranged from low to moderate compared to WHO limits of 5.0 mg/kg in the order AR>BR>CR. Cd and Mn for all other sites were moderate compared to WHO standard (0.20 and 5.50 mg/kg respectively) and was in the order; CR>BR>AR. The increased heavy metals concentration from all sites suggest that fishes that inhabit polluted areas risk bioaccumulation, which go on to affect the overall health of the human population within the area.*

Keywords: *Catfish, Bioaccumulation, Pond, River, Pollution.*

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I. Introduction

Several water bodies present in different parts ofthe world have been polluted by anthropogenic activities. The pollutants are in form of pesticides, heavy metals, personal care products, pharmaceuticals (Mahino*et al*., 2014), and in recent times, oil spills frequently occurring as a result of the world's increased use of petroleum as main source of energy.

The rapid development of crude oil exploration and transportation is known to increase the tendency for an oil spill incidence to occur which in turn releases heavy metals and poly aromatic hydrocarbons among other things into surrounding waters and the environment.

The exploration of petroleum products has rendered agricultural lands less productiveand the creeks and the aquatic lives have become more or less dead (Nwauche *et al.,* 2018).

Oil spillage occurs when crude oil or other products derived from it, leaks accidentally on land or water when transported or distributed resulting in environmental pollution. Incidence of crude oil spills has been recorded in different parts of the world, where it has been noted that it often generates serious problems to the environment in these parts, (Adesina *et al*., 2013). Nigeria as a major exporter of crude oil has experienced crude oil spills which affected agricultural lands as well as plant growth and development in the areas affected (Agbogidi*et al*., 2005), with the Niger delta regions at the receiving end of such oil exploration in the country. Several studies on oil spills and environment in the Niger Delta area and other tropical areas throughout the world consistently showed that areas that are directly exposed to large or repeated oil spills or leaks frequently exhibit long-term environmental problems (Amadi *et al*., 1996, Obire, 1988).

Pollution on water bodies by PAHs is caused by petroleum spills, and other man-made activities such as; discharges and seepages, industrial and municipal waste water, urban and suburban surface runoffs, and atmospheric deposition, (Eisler, 2000). Meanwhile, presence of heavy metals in the environment could occur as a result of; industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources, (He*et al*., 2005). Environmental pollution could be point source or non-point source, but is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operation, (Fergusson, 1990; He *et al*., 2005).

The impact of heavy metals on aquatic organisms is due to the movement of potential pollution causing substances from various point sources which give rise to coincidental mixtures in the ecosystem (Anderson and Appollonia,1978), thus posing a serious threat to aquatic organisms especially to fishes which constitute one of the major sources of protein-rich food for mankind.

Fishes are continuously exposed to pollutants in the water, due to continuous water flow through gills and food and it has been discovered that fish are able to accumulate several fold higher concentration of pollutants than the surrounding water (Law and Hellou, 1999, Vives*et al*., 2004, Johnson-Restrepo*et al*., 2008).

II. Materials And Methods

Collection of Fish sample

The eighteen (18) African catfish (*C.gariepinus*) used in this study were collected from Akaraolu swamps,Akaraolu village in Ahoada East LGA, Rivers state (AR)(The village land and swamps are known to be within the area heavily polluted by crude oil due to explorations taking place by AGIP), the New Calabar River within Ikwerre LGA, Rivers state (BR), Omambala River in Aguleri, Anambara East LGA, a distributary of the River Niger (CR), a commercial fish pond within Ahoada-East LGA in Rivers state (AP), a commercial fish pond established close to one of the distributaries of the New Calabar River in Omuihuechi village in Ikwerre LGA, Rivers state (BP), a commercial fish pond in Awka, Anambara state (CP). Three samples were collected from each of the above named sites andkept in large containers holding water from the sample sites to keep thefishes in their original habitat so as not to alter parameters under study. On arrival, the fish samples were sacrificed, wrapped in an aluminium foil and transferred to Dexcom Solutions Limited at 458 Ikwerre road, Block 2, flat 1 Woherem Estate, Rumuokwuta, PortHarcourt, Nigeria, for homogenized heavy metals and Polycyclic aromatic hydrocarbons assay.

The heavy metals and polycyclic aromatic hydrocarbons were assayed following standard procedures.

Heavy metals analysis

The following metals; Cadmium, Chromium, Nickel, Lead, Magnesium, and Zinc were analyzed using an Atomic Absorption Spectrophotometer (Agilent 200 series AA (240 AA)) in a three step process;

Acidification

Fresh fish samples were washed and cleaned with distilled water for the removal of external dirt. The samples were then dissected using solvent rinsed instruments and glass dishes.The dissected samples were minced with aid of a blender into small pieces and stored in air tight containers. The samples were then dried to constant weight at $<60^{o}$C and homogenized.From the homogenized samples, 5g was measured into a digestion flask. 20ml of prepared HCl and HNO_3 (3:1) was added into the digestion flask and was sent for digestion.

Finishing (digestion)

The digestion flask containing the samples and the acids were then heated on a hot plate in a well-ventilated hood until the volume had been reduced to 5ml, making certain that the sample did not boil.The heated sample was then cooled and filtered into a 100ml volumetric flask and the volume adjusted to mark with the use of distilled water.The diluted sample was then transferred into sample bottles for assay with an atomic absorption spectrophotometer.

Analysis with atomic absorption spectrophotometer

The heavy metals were determined using an Atomic Absorption Spectrophotometer (AAS) as described in APHA 3121B/3112B and ASTMD 3651. This involved direct aspiration of the sample in air/acetylene flame and a hollow cathode lamp analyzes the sample at a specific wavelength peculiar to the desired metal. For every metal investigated, standards and blanks were prepared and used for calibration before samples were aspirated and concentrations at specific absorbance displayed on the data system monitor for printing. The concentration in mg/kg dried weight were determined (after analysis) using the weight and volume of the samples.

Polycyclic aromatic hydrocarbons

About sixteen PAHs were analysed using an Agilent 7890BGC/MSD5977A Gas chromatograph. In the process, fresh fish samples are washed with distilled water to remove external dirt. They were then dissected using solvent rinsed instruments and glass dishes. The dissected samples are then minced into smaller pieces with the aid of a blender and kept in an air-tight container.20g of blended sample was put into a clean 120ml amber bottle, after which 20ml of MeOH/KOH solution was added to amber bottle. The mixture was then heated in a water bath for 30mins at 60^{o}C for saponification. After which it was kept standing and allowed to cool.

Extraction

For the process of extraction, the saponified sample was filtered through glass wool into a 500ml separating funnel, to which 100ml of hexane was then added to the sample and was rocked for 3minutes. The hexane layer was transferred into a conical flask into which 100ml of hexane was again added and rocked for another 3mins.The hexane layer was washed by shaking with 50ml MeOH/H_2O solution for 1min. The washing was repeated two or more times.The extract was then evaporated to 2ml and cleaned up.

Clean Up

Activated silica gel heated overnight at 130^oC was placed in 50ml Methylene Chloride to make slurry. The slurry was then poured into a 10mm diameter chromatography column. Then the column was gently tapped to settle the silica gel and elute with 30ml Methylene Chloride. A 1cm layer of anhydrous sodium sulphate was then added to the top of the silica bed.The column was pre-eluted with 60ml hexane, which was then discarded before exposure of sodium sulphate to the air.The 2ml of extract exchange was the transferred to the column together with the hexane.Prior to the exposure of the sodium sulphate layer to the air, the column was eluted with 25ml of methylene chloride and the elute collected into a beaker for Aromatic (PAH) analysis. This was then allowed to concentrate to 2ml, then transferred into a Teflon screw cap vial well labeled, after which it then proceeded for GC analysis of PAH.

Analysis of PAHs using a gas chromatogram

PAHs analysis was carried out in line with EPA 8270 method using Agilent 7890BGC/MSD5977A equipped with an auto-sampler, a split injector, J and WDB-5, 30m x 0.25mm id, 0.25µm column and Mass Selective Detector. The total run time was 33.75 minutes. The GC was calibrated using five working standards prepared from a stock solution of Accu standard for PAH of 2.0mg/ml in Dichloromethane: Benzene (1:1).

III. Results

The results for the concentrations of carcinogenic and non-carcinogenic PAHs, and heavy metals in catfish from oil and non-oil polluted areas in Rivers and Anambra states are given in Table 1,2, and 3 below.

The benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene,benzo(a)pyrene, indeno(1,2,3-Cd)pyrene, and diben(a,h)anthracene concentrations from AR (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively) were not significant from the benzo(a)enthracene, chrysene, benzo(b)fluorenthene, benzo(k)fluorenthene, benzo(a)pyrene, indino(1,2,3-Cd)pyrene,anddiben(a,h)anthracene concentrations of BR(0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively) and CR (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively).

Also the benzo(a)anthrecene, chrysene, benzo(b)fluorenthene, benzo(k)fluorenthene, benzo(a)pyrene, indeno(1,2,3-Cd)pyrene, and diben(a,h)anthracene concentrations from AP (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively) were not significant compared to those in BP (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively) and CP (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively).

Table 1: Carcinogenic Polycyclic aromatic hydrocarbon concentrations of homogenized catfish from oil polluted swamps, non-oil polluted rivers and commercial fish ponds within oil polluted areas and non-oil polluted areas in Rivers and Anambra states.

PAHS	AR	BR	CR	AP	BP	CP
Benzo(a)anthracene	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^c	0.01 ± 0.001^c	0.01 ± 0.001^c
Chrysene	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^c	0.01 ± 0.001^c	0.01 ± 0.001^c
Benzo(b)fluoranthene	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^c	0.01 ± 0.001^c	0.01 ± 0.001^c
Benzo(k)fluoranthene	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^c	0.01 ± 0.001^c	0.01 ± 0.001^c
Benzo(a)pyrene	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^c	0.01 ± 0.001^c	0.01 ± 0.001^c
Indeno(1,2,3-cd)pyrene	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^c	0.01 ± 0.001^c	0.01 ± 0.001^c
Diben(a,h)anthracene	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^a	0.01 ± 0.001^c	0.01 ± 0.001^c	0.01 ± 0.001^c

Values are means ± S.D. Values with different superscript are statistical significant at ($P < 0.05$). BR and CR were compared to AR while BP and CP were compared to AP. Superscript (a,b) compares BR and CR to AR while Superscript (a, b, c,d) compares BP and CP to AP.

Table 2 shows the non-carcinogenic polycyclic aromatic hydrocarbon concentrations of homogenized catfish from AR, BR, CR, AP, BP and CP.The naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoroanthene, pyrene, and benzo(g,h,j)perylene concentrations of AR (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001,0.01 ± 0.001 and 0.01 ± 0.001 respectively) were

not significantly different from those from BR (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively) and CR (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001 and 0.01 ± 0.001 respectively). The concentration of anthracene from CR (0.05± 0.03) was significantly higher than those from AR (0.01± 0.001) and BR (0.01±0.001)
Also the naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, fluoroanthene, pyrene, and benzo(g,h,j)perylene concentrations from AP (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001,0.01 ± 0.001 and 0.01 ± 0.001 respectively) were not significantly different from those from BP (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, and 0.01 ± 0.001 respectively) and CP (0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001, 0.01 ± 0.001 and 0.01 ± 0.001 respectively).While the concentration of anthracene from CP (0.05± 0.01) was significantly higher than those from AP (0.01± 0.001) and BP (0.01±0.001).

Table 2: Non-carcinogenic Polycyclic Aromatic Hydrocarbon concentrations of homogenized catfish from oil polluted swamps, non-oil polluted rivers and commercial fish ponds within oil polluted and non-oil polluted areas in Rivers and Anambra states.

PAHS	AR	BR	CR	AP	BP	CP
Naphthalene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]
Acenaphthylene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]
Acenaphthene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]
Fluorene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]
Phenanthrene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]
Anthracene	0.01±0.001[a]	0.01±0.001[a]	0.05±0.003[b]	0.01±0.001[c]	0.01±0.001[c]	0.05±0.003[d]
Fluoroanthene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]
Pyrene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]
Benzo(g,h,j)perylene	0.01±0.001[a]	0.01±0.001[a]	0.01±0.001[a]	.01±0.001[c]	0.01±0.001[c]	0.01±0.001[c]

Values are means ± S.D. Values with different superscript are statistical significant at ($P < 0.05$). BR and CR were compared to AR while BP and CP were compared to AP. Superscript (a,b) compares BR and CR to AR while Superscript (c,d) compares BP and CP to AP.

Description of variables:AR: Catfish from Akaraolu swamps Ahoada East LGA, oil polluted area, BR: The New Calabar River, Ikwerre LGA, non- oil polluted area, CR: OmambalaRiver Anambra East LGA, a non-oil polluted area. AP: commercial fish pond, Ahoada East LGA, oil polluted area, BP: commercial fish pond in Ikwerre LGA, non-oil polluted area, CP: commercial fish pond in Awka, Anambra state, non-oil polluted area.
Table 3 shows heavy metal concentrations of homogenized catfish AR in comparison to BR and CR, also AP, in comparison to BP and CP. The concentrations of Ni, Zn and Cr (0.77±0.13, 5.65 ± 0.11, and 27.73 ± 1.79 respectively) from AR were significantly different from Ni, Zn and Cr (3.76±0.33, 4.15 ± 0.07, and 46.20 ± 0.64 respectively) from BR. The concentrations of Pb, Cd and Mn (3.33 ± 0.29, 0.26 ± 0.01 and 0.38 ± 0.02 respectively) from BR were not significantly ($p<0.05$) different from AR (2.60 ± 0.31, 0.29 ± 0.01and 1.30 ± 0.16 respectively).The concentration of Ni, Zn, Cd, Cr, and Mn (0.77±0.13, 3.33±0.29, 5.65±0.11, 0.26±0.01, 27.73±1.79, and 0.38±0.02 respectively) from AR were significantly different from Ni, Pb, Cd, Cr, and Mn (4.54±0.20, 3.87±0.18,22.83±0.16, 2.05±0.01, and 24.26±1.32 respectively) from CR, while the concentration of Pb (3.33 ± 0.29) from AR was not significantly different (3.87 ± 0.18) from CR. The concentration of Ni, Pb, and Zn (2.23±0.09, 4.13±0.24, and 3.07±0.51 respectively) from AP were not significantly different from Ni, Pband Zn (3.04±0.50, 4.67±0.29, and 2.14 ± 0.05 respectively) from CP as shown in Table 4.3. While Cd, Cr, and Mn (0.21±0.01, 24.13±0.60, and 0.31±0.04 respectively) from AP were significantly different from Cd, Cr, and Mn (2.24±0.12, 43.49±0.80, and 21.79±0.88 respectively) from CP.The concentration of Ni, Pb, Cd, Zn, and Mn (2.23±0.09, 4.13±0.24, 3.07±0.51, 0.21±0.01 and 0.31±0.04 respectively) from AP were significantly different from BP (2.85±0.21, 2.87±0.48, 2.96±0.37, 0.22±0.01, and 1.99±0.02 respectively). While concentrations of Cr (24.20±0.60) from AP was significantly different from BP (44.24±3.05).

Table 3 Heavy metal concentrations of homogenized catfish from oil polluted swamps, non-oil polluted rivers and commercial fish ponds within oil polluted and non-oil polluted areas in Rivers and Anambra states.

H/M	AR	BR	CR	AP	BP	CP	WHO/L
Ni(mg/kg)	0.77±0.13[a]	3.76±0.33[b]	4.54±0.20[b]	2.23±0.09[c]	2.85±0.21[c]	3.04±0.50[c]	0.50
Pb(mg/kg)	3.33±0.29[a]	2.60±0.31[a]	3.87±0.18[a]	4.13±0.24[c]	2.87±0.48[c]	4.67±0.29[c]	0.40
Zn(mg/kg)	5.65±0.11[a]	4.15±0.07[b]	2.83±0.16[b]	3.07±0.51[c]	2.96±0.37[c]	2.14±0.05[c]	5.00
Cd(mg/kg)	0.26±0.01[a]	0.29±0.01[a]	2.05±0.01[b]	0.21±0.01[c]	0.22±0.01[c]	2.24±0.12[d]	0.20
Cr(mg/kg)	27.73±1.79[a]	46.20±0.64[b]	52.59±1.32[b]	24.13±0.12[c]	44.25±3.05[d]	43.49±0.80[d]	1.00
Mn(mg/kg)	0.38±0.02[a]	1.30±0.16[a]	24.26±1.32[b]	0.31±0.04[c]	1.99±0.02[c]	21.79±0.88[d]	5.50

Values are means ± S.D. Values with different superscript are statistical significant at ($P < 0.05$). BR and CR were compared to AR while BP and CP were compared to AP. Superscript (a,b) compares BR and CR to AR while Superscript (c,d) compares BP and CP to AP.
Description of variables: H/M: heavy metals, NI: nickel, Zn: zinc, Cd: cadmium, Cr: chromium, Mn: manganese**.**AR: Catfish from Akaraolu swamps Ahoada East LGA, oil polluted area, BR: The New Calabar River, Ikwerre LGA, non- oil polluted area, CR: Omambala River, Anambra East LGA, a non-oil polluted area. AP: commercial fish pond, Ahoada East LGA, oil polluted area, BP: commercial fish pond in Ikwerre LGA, non-oil polluted area, CP: commercial fish pond in Awka, Anambra state, non-oil polluted area.

IV. Discussion

Polycyclic aromatic hydrocarbons are a class of hydrocarbons that have above two aromatic rings fused together. They can have methyl, ethyl or alkyl group substituting one of its hydrogen. In some cases sulphur, oxygen, or nitrogen can also substitute one or more of its carbon atoms (Incardona*et al*., 2005). Exposure to PAHs may lead to changes in DNA methylation in fish (Fang *et al*., 2010), including changes associated with carcinogenesis (Fang*et al*., 2010; Mirbahai*et al*., 2011). Changes in DNA methylation in liver neoplasms have been observed in both laboratory-reared zebrafish, in which tumors were induced with a model carcinogen (Mirbahai*et al*., 2011), and wild dab that developed neoplasms as a result of environmental exposure to PAHs (Mirbahai*et al.*, 2011). In this study, the concentrations of carcinogenic and Non-carcinogenic PAHs; benzo(a)anthrecene, chrysene, benzo(b)fluorenthene, benzo(k)fluorenthene,benzo(a)pyrene, indeno(1,2,3-Cd)pyrene, and diben(a,h)anthracaneandnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoroanthene, pyrene, and benzo(g,h,j)perylene in Catfish from all sites though low, however, are reflective that pollution could affect aquatic lives via bioaccumulation in oil polluted areas. These results agree with the report of Ikue et al., 2016 on the accumulation of PAHs in tissues of catfish *Chrysichthysgrodidatatus*from crude oil tainted water of Ogoni, River State, Nigeria.

The accumulation of toxic metals to hazardous levels in aquatic biota has become a problem of increasing concern. This is because it has a direct and almost non escapable effect on man, either by drinking the water, using it as irrigation or by consuming the fishes from it (Mathis and Cummings, 1973). In this study, the Ni concentration from all the crude oil polluted and non-oil polluted sites ranged from 0.77±0.13, 3.76±0.33, 4.54± in the 0rder (CR>BR>AR) and were greater than the WHO permissible limits (0.5mg/kg) for Ni in fish tissues. The same trend was also noticed in fishes harvested from the commercial fish ponds from all sites in the decreasing order (CP>BP>AP) with higher concentrations in fishes from the commercial pond in Awka. The Pb concentration from both crude oil polluted and non-crude oil polluted sites was also higher than the WHO/FAO (FAO, 2003) permissible limits of 0.4mg/kg. The values ranged from 3.87±0.18, 3.33±0.29, 2.60±0.31, in the order (CR>AR>BR). The lead concentrations for fishes from commercial fish ponds ranged from 4.67±0.29, 4.13±0.24, and 2.87±0.48 in the order CP>AP>BP and this was also greater than the WHO permissible limits for Pb (0.4mg/kg). The Zn concentration ranged from moderate to low concentration in comparison to the WHO permissible limits of 5.0mg/kg with the Zn concentration for fishes from the oil polluted site in Akaraolu swamps been highest at 5.65±0.11. Zn values from ponds were lower than the WHO permissible limits of 5.0mg/kg as shown in Table 4.3.Concentrations of cadmium was highest for fishes harvested from the Omambala River, Anambra, with values 2.05±0.01 in comparison to the other sites in Akaraolu swamps and the New Calabar River which had moderate values in comparison to the WHO permissible limit for Cd. Also for the ponds, fishes from Awka (CP) had values (2.24±0.12) greater than the WHO permissible limits in comparison to the others which were just within range. Chromium concentration was high in comparison to the WHO limit (1.00mg/kg) for all sites with values differing in the order CR>BR>AR. The same was recorded for the Cr concentration for fishes from ponds in crude oil polluted and non-crude oil polluted sites. All values were above WHO limit. Manganese concentration for fishes from the New Calabar River and Akaraolu swamps were below the WHO permissible limit of 5.5mg/kg, unlike that from the Omambala River which was higher. Also the same trend was witnessed in the Mn concentration for fishes from commercial fish ponds surveyed, with values from the ponds in Awka (CP) been higher. The increased concentration of heavy metals deposition in fishes from The Omambala River have been attributed to anthropogenic activities, also agricultural activities involving use of fertilizers, as well as poor sewage disposal into the river (Ujah*et al.*, 2017). The increased heavy metal accumulation in fishes from Omambala River, a distributary of the River Niger Onitsha, Anambra state segment supports the findings by Ujah*et al.*, 2017, on pollution in the River/fishes in the River Niger, Onitsha, Anambra state segment. The heavy metals accumulation in fishes from the New Calabar River also supports the finding by Nwankwo and Angaya (2017), that the New Calabar River, Choba segment was polluted by heavy metals both water and sediments . Generally, the results from all sites also support the report of Mohammed, 2009 on the accumulation of heavy metals in tilapia fish (*Oreochromisniloticus*) from Al-Khadoud Spring, Al-Hassa, Saudi Arabia.

V. Conclusion

The data generated from this study showed that there were actually heavy metals accumulations in fish tissues from all Rivers which were higher than those from the commercial fish ponds sampled, and were above the WHO permissible limits for most of the metals sampled. The accumulation of metals sampled were in the decreasing order; Cr>Mn>Zn>Pb>Ni>Cd. Also results showed a presence of carcinogenic and non-carcinogenic PAHs in the catfish tissues, although they were at low concentrations. This still poses a danger if accumulation was to take place over a long period of time.

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