## Selective Bioaccumulation of Metals by Different Parts of Some Fish Species from Crude Oil Polluted Water

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Oil discovery in the Niger Delta region of Nigeria since 1958 is responsible for Nigeria's ranking as the sixth largest producer of crude oil in the world. An inevitable effect is the millions of barrels of crude oil spills. The environment worst affected include salt marshes, mangrove swamps, coral reefs, shellfish beds, fish hatcheries and any stagnant waters without good dilute factor (SPDC, Nigeria 1997). This is associated with pollutant effects from the use of chemicals such as dispersants and corrosion inhibitors. The recent discovery that water samples taken from eighteen (18) different sites from boreholes wells, lagoons and beaches of Niger Delta region contains carcinogen — Benzo (a) Pyrene, an alternate polynuclear hydrocarbon in high concentration ranging from 0.43-4mg/I far above the World Health Organization (WHO) stipulated 0.7mg/I standard for drinking water, thereby exposing the people to skin, lung, breast and abdominal cancer (Akanimo, 2005). Nigeria's crude is known to associate with different proportions of heavy metals which vary from a few ppm (mg/l) to more than 1000ppmm (Nelson, 1958).

Metals contribute to the diversity of toxic pollutants that can damage the ecosystem (Othmer, 1968). Trace metals in crude oils and other bituminous substances worldwide have been recognized (Nwadinigwe and Nworgu, 1999, Handson, 1994, Barwise, 1994). Crude oil release these metals into the aquatic environment and they find their way into food chain via lugworms, barnacles and planktons which fish feed on (SPDC, Nigeria 1997, Bunmi, 2004). It is estimated that more than four thousand (>4,000) oil spills have occurred in the Niger Delta region of Nigeria since 1960 releasing several million barrels of crude oil (containing heavy metals) into the interwoven water bodies of the Niger Delta (Nnaemeka, 2005).

These metals are classified as toxic water pollutants as they bio-accumulate on the fishes upon which the local populace depend for their daily upkeep (Bob,1990). This work was carried out to ascertain if there is a correlation between oil spillages in the study area and heavy metal concentration in the different fish parts analysed. Water samples, soil sediments and water weed (water hyacinth) from the same river were also assayed for comparative assessments.

Table 1. Preliminary data on fish samples.

Fish species	Length of body (cm)	Total body weight (g)	Total brain weight (g)	Total Gill weight (g)	Total Flesh weight (g)	Total intestine weight (g)
Tilapia niloticus	21	135.0	0.2	6.9	82.7	6.9
Gynchus niloticus	40	302.3	0.2	11.3	266.2	5.7
Chrysichthys auratus	18	42.8	0.1	1.4	22.1	5.5
Ethmaliosa timbriata	9	12.4	<0.1	0.1	8.6	0.9

## MATERIALS AND METHODS

Four different fish species, water sample, soil sediments and water hyacinth were collected from Oduaoha River (River with long history of oil spills) in Emuoha Council Area of River State (Second largest oil producing state) in Nigeria. All the samples were collected early in the morning with the assistance of local fishermen. The fish samples were first separated into parts with a clean table knife. The parts were ashed at a temperature of 500°c for 3hrs. The residue was digested with HNO3: HCIO4 (5.:3) mixture. For all the brain, 0.03g-0.1g of the residue was weighed into a beaker; 10ml of HNO3 was added then the sample was heated at a relatively low temperature until the beaker content reduced to half. It was allowed to cool before the addition of 6ml of HClO<sub>4</sub>. The heating was repeated until a clear solution was obtained. It was allowed to cool and filtered. The filtrate was made up to 100ml mark using de-ionised water. The same procedure was repeated for other parts as follows: 0.1g or 5g of gill of fish/10ml or 20ml solution, 5g of flesh of fish/20ml solution and 0.8 or 5g of intestine of fish/10ml or 20ml of solution. 5g of water hyacinth/20ml solution and 2g of bottom sand/15ml solution. Concentrations of the metals were determined using Atomic Absorption Spectrophotometer 200A.

## **RESULTS AND DISCUSSION**

Table 2. Metal Concentration in Fish Parts (mg/kg).

Samples	Pb	Zn	Cu	Ni	Cd	Co	Cr	Fe	Mn
Tilapia niloticus, Brain	5	194.9	108.0	56.3	1.6	<0.1	24.0	792.3	15.4
Gill	6	34.4	5.1	1.5	0.4	0.6	0.8	412.9	9.1
Flesh	0.5	12.1	2.9	5.0	0.1	0.3	<0.1	34.2	1.0
Intestine	5.5	22.0	4.6	8.5	0.3	2.6	4.8	2010.5	36.4
Gynchus niloticus Brain	<0.1	89.1	60.0	<0.1	<0.1	<0.1	4.0	338.5	7.7
Gill	0.8	25.1	1.0	0.8	0.3	0.6	1.0	74.5	1.5
Flesh	1.0	17.8	3.7	0.8	0.2	<0.1	0.8	14.2	1.5
Intestine	0.3	29.9	7.0	5.0	0.3	0.3	0.3	301.2	7.2
Chrysichthy s auratus Brain	<0.1	154.5	14.0	<0.1	<0.1	<0.1	24.0	376.9	16.3
Gill	7.5	55.8	6.0	0.6	0.3	3.6	0.8	592.3	9.4
Flesh	0.5	22.0	4.6	2.0	0.1	0.3	<0.1	20. 9	1.1
Intestine	0.5	76.7	6.0	3.3	0.1	0.9	<0.1	104.9	2.2
Ethmaliosa timbriata brain	<0.1	285.2	198.3	97.7	<0.1	<0.1	79.5	1409.1	41.0
Gill	0.8	18.2	3.2	0.6	0.2	1.4	<0.1	56.9	2.9
Flesh	1.0	42.9	13.7	5.8	0.3	0.9	0.3	37.5	4.6
Intestine	<0.1	49.0	9.1	1.5	<0.1	<0.1	<0.1	124.6	4.4

Table 3. Total metal concentration in mg/kg of fish

(Derived from table 2).

Pb	Zn	Cu	Ni	Cd	Со	Cr	Fe	Mn
17	263.4	120.7	71.3	2.3	3.5	29.7	3,249.8	61.8
2.2	161.9	71.6	6.6	0.9	1.1	6.1	728.3	18.0
8.6	309.0	30.7	6.0	0.6	4.8	25.0	1095.5	29.1
2.8	395.3	224.3	105.5	0.6	2.5	80.0	1628.1	52.9
	2.2	17 263.4 2.2 161.9 8.6 309.0	17 263.4 120.7 2.2 161.9 71.6 8.6 309.0 30.7	17     263.4     120.7     71.3       2.2     161.9     71.6     6.6       8.6     309.0     30.7     6.0	17     263.4     120.7     71.3     2.3       2.2     161.9     71.6     6.6     0.9       8.6     309.0     30.7     6.0     0.6	17     263.4     120.7     71.3     2.3     3.5       2.2     161.9     71.6     6.6     0.9     1.1       8.6     309.0     30.7     6.0     0.6     4.8	17     263.4     120.7     71.3     2.3     3.5     29.7       2.2     161.9     71.6     6.6     0.9     1.1     6.1       8.6     309.0     30.7     6.0     0.6     4.8     25.0	17     263.4     120.7     71.3     2.3     3.5     29.7     3,249.8       2.2     161.9     71.6     6.6     0.9     1.1     6.1     728.3       8.6     309.0     30.7     6.0     0.6     4.8     25.0     1095.5

**Table 4.** Average metal concentration in mg/kg (Derived from Table 2).

	Pb	Zn	Cu	Ni	Cd	Co	Cr	Fe	Mn
Tilapia niloticus	4.3	65.3	30.2	17.8	0.6	0.9	7.4	812.5	15.5
Gynchus niloticus	0.6	40.5	17.9	1.7	0,2	0.3	1.5	182.1	4.5
Chrysichthys auratus	2.2	77.2	7.7	1.5	0.2	1.2	6.3	273.8	7.3
Ethmaliosa timbriata	0.7	98.8	56.1	26.4	0.2	0.6	20.1	407.0	13.2

Table 5. Metal concentration in mg/l in water sample

Sample	Pb	Zn	Cu	Ni	Cd	Co	Cr	Fe	Mn
Odua-Oha water	0.01	0.13	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Table 6. Average metal concentration in mg/kg of solid sample.

Samples	Pd	Zn	Cu	Ni	Cd	Со	Cr	Fe	Mn
Bottom Sand	<0.01	0.45	0.02	<0.01	0.01	0.01	<0.01	14.65	0.16
Water Hyacinth	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.36	0.60

Table 7. Heavy metal contents of marine fish from lagos lagoon (Mean std) mg/kg (Tomori, Aivseanmi and Obijola 2004

Samaple	Cd	Zn	Pb	Cu	Ni	Mn	Со	Cr
Cyoglossus Senegalensis	ND	0.82 (±0.16)	ND	0.22 (±0.05)	0.01 (±0.0 1)	0.28 (±0.03)	0.11 (±0.02)	0.25 (±0.05)
Galeoides Decafacty lus	ND	0.95 (±0.32)	0.22 (±0.0 2)	0.22 (±0.03)	0.03 (±0.0 2)	0.12 (±0.02)	0.10 (±0.03)	ND
Ilisha Africana	0.01 (±0.0 1)	2.42 (±0.53)	0.09 (±0.0 2)	0.01 (±0.01)	0.09 (±0.0 3)	0.25 (±0.06)	0.05 (±0.03)	0.76 (±0.25)
Sphyraema Piscatorum	ND	0.91 (±0.30)	0.01	0.01 (±0.01)	0.71 (±0.2 7)	0.10 (±0.02)	ND	ND
Seudolit Senegalensis	0.05 (±0.0 2)	8.76 (±0.01)	0.14 (±0.0 3)	0.17 (±0.01)	ND	0.12 (±0.01)	ND	ND
Pseudolith Elongates	0.03 (±0.0 2)	2.46 (±0.62)	0.09 (±0.0 5)	0.25 (±0.07)	0.41 (±0.0 8)	0.14 (±0.01)	ND	0.56 (±0.02)
Drepane Africana	0.01 (±0.0 1)	1.10 (±0.28)	ND	0.12 (±0.06)	0.04 (±0.0 1)	0.19 (±0.06)	0.01 (±0.01)	ND
Chloroscrom brus Chrysurus	0.01 (±0.0 1)	1.87 (±0.42)	0.13 (±0.0 3)	0.21 (±0.0)	ND	0.05 (±0.02)	0.01 (±0.02)	0.13 (±0.08)
Vomer Setapinnis	ND	0.59 (±0.18)	0.13 (±0.0 7)	0.13 (±0.06)	0.08 (±0.0 4)	0.07 (±0.01)	0.08 (±0.02)	0.13 (±0.02)
Brachydeute rus Auritus	0.02 (±0.0 2)	4.64 (±0.42)	0.11 (±0.1 0)	0.23 (±0.04)	0.01 (±0.0 2)	0.12 (±0.04)	0.01 (±0.01)	0.59 (±0.16)

Table 8. Mean concentration of metals in mg/kg of fish From Rima River in Sokoto (Abdulrahman and Tsafe, 2004).

Samples	Pb	Cd	Ni	Mn	Fe	Zn
Tilapia	0.708	0.001	0.032	0.029	1.132	0.070
Begrus bayed	0.669	0.008	0.060	0.018	2.284	1.85
Synodontis clarias	0.738	0.013	0.182	0.017	0.923	0.04

Table 9. Heavy metal contents in mg/kg of fish from other countries of the world [(Jorhem and sundstrom, 1993), Odukoya and Ajayi (1987a), (1987b)].

Samples	Cu	Zn	Pb	Cd
Australia commercial fish	0.01-2.4	0.90-24	-	0.03-0.10
USA Portsmouth seafish (shell-fish)	1.45-2.10	14. 9-15. 9	1.21-1.76	0.4-3. 06
Greece sea fishes  Polluted Areas muscle Unpolluted Area Muscle	1.00-1.70 0.89-1.3	37-71 48-58	-	<0.3 <0.3
Israel Haife Sea Fishes	0.7-23.5	0.50- 84.30	0.30-5.30	0.10-0.70
Gulf of Mexico and Bahawa Islands	0.23-1.15	3.17-40.00	0.05-0.73	0.01-0.09
West Malaysia coastal water fishes	-	2.30-6.50	0.21-0.32	0.03-0.05
Swedish EPB Lake Fishes Music	0.30-2.02	0.10-0.15	0.045-0.181	0.012-0.4 5
Swedish market	0.13-0.73	2.2-17.0	0.005-0.014	<0.001- 0.008

Table 10. FA0/WHO standard for metal content in mg/kg in fish muscles.

Pb	Cd	Ni	Fe	Zn	Mn
0.2	0.05-0.2	0.1-0.9	1.0-4.5	5.0-10	0.5-1.2

Results displayed in table 2,3,4,5 and 6 above are very instructive. The brain of the four fish species has higher concentrations of zinc (Zn), Copper (Cu), Nicked (Ni), Chromium (Cr) Manganese (Mn). The brain of Tilapia niloticus, Gymanachus niloticus and Ethmalosa timbriatat has highest iron (Fe) content. The gill of chrysichthys auratus has the highest concentration of lead (Pb), Cobalt (Co) and iron (Fe) and the intestine Nickel (Ni). From tables 3 and 4, a trend can be established, thus:

Tilapia niloticus Fe>Zn>Cu>Ni> Mn>Cr> Pb> Co>Cd, Gynchus niloticus Fe>Zn>Cu>Mn>Ni>Cr>Pb>Co>Cd, Chrysichthys auratus Fe>Zn>Cu>Ni>Cr>Mn>Pb>Co>Cd, Ethmaliosa timbriata Fe>Zn>Cu>Ni>Cr>Mn>Pb>Co>Cd,

It is significant that, of all parts examined, the brain has the greatest affinity (though with minor variations) for Fe, Cu, Zn, Ni, Cr, and Mn. Generally, in all the sample, iron and cadnium occurred highest and least. When these values are compared with those of Tables 7 and 8 (from non-oil bearing regions of Nigeria (Tomori et al 2004, Abbudlrahman and Tsafe, 2004), those of some other countries of the world (table 9, though fish species vary) (Jorhen and Sundstrom, 1993) and some FAO/WHO standard (table 10), it is evident that the samples of study are highly contaminated with the metal assessed implying that a person who consumes fish from the study area would likely be exposed to metal poisoning and health risk associated with them. This makes the hospitality industry where these fish are coveted delicacies unattractive. When the results are also compared with Tables 5 and 6 (other test samples from the same River), it proves that water pollutants mainly affect aquatic animals as against water itself, soil sediment and water weeds. Low values recorded for the bottom sediments may be attributed to the sand excavation by the inhabitants which does not readily allow for metal accumulation.

Though heavy metal contamination of water bodies may be from other sources such as automobiles, nature of basement rocks, industrial processes and, in some cases, agricultural practices, the comparison of previous studies (Tables 7 and 8) shows that high proportion of the metals must be from crude oil spills which is a regular occurrence in the Niger Delta region of Nigeria. This exposes the local populace (who are mainly fishermen and sand excavators), the larger Nigerian people and visitors (tourists) who may consume the fish to health risks.

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