Original Research Article

EVALUATION OF THE LEVELS OF HEAVY METALS, TOTAL PETROLEUM HYDROCARBON AND TOTAL HYDROCARBON CONTENT IN *Tympanotomus fuscatus* AND SEDIMENT, QUA IBOE RIVER, AKWA IBOM STATE, NIGERIA.

Abstract

This study assesses the levels of heavy metals and hydrocarbons in *Tympanotomus fuscatus* and the sediments of Qua Iboe River, Akwa Ibom State; the interest in the study area was due to the several industrial and oil exploration activities in the area. The heavy metals (HM) of interest were Pb, Cd, Cu, Se, Zn, As, Cr, Fe, Ni and Hg, determined using Atomic Absorption Spectroscopy while Total Hydrocarbon Content (THC) and Total Petroleum Hydrocarbon (TPH) were determined by the GC-FID method. Results obtained indicated that the heavy metal concentration in *Tympanotomus fuscatus* ranged as follows: Pb (1.037 – 2.002 mg/kg), Cd (0.00 – 0.088 mg/kg), Cu (0.0037 – 10.01 mg/kg), Se (2.364 – 5.063 mg/kg), Zn (0.025 – 1.393 mg/kg), As (0.0113 – 0.355 mg/kg), Cr (1.075 – 3.055 mg/kg), Fe (2.384 – 10.022), Ni (0.045 – 1.223 mg/kg), Hg (0.037 – 1.003 mg/kg) while heavy metal concentration in sediments were: Pb (1.399 – 2.345 mg/kg), Cd (0.0267– 0.222 mg/kg), Cu (0.017 – 10.0197 mg/kg), Se (1.388 – 3.369 mg/kg), Zn (5.688 – 8.038 mg/kg), As (0.003 – 0.0317 mg/kg), Cr (0.0157 – 2.057 mg/kg), Fe (27.351 – 86.686), Ni (0.017 – 5.0413 mg/kg), Hg (0.06 – 1.53 mg/kg); generally, heavy metals levels were higher in dry season than in wet season. The levels of TPH ranged from 160.86 – 1081.52 mg/kg in *Tympanotomus fuscatus* and 175.97 – 3143.91 mg/kg in sediments; meanwhile, the concentration of TPH ranged from 728.47 – 2442.04 mg/kg in *Tympanotomus fuscatus* and 492.41 – 7186.25 mg/kg in sediments. Multiple

correlation coefficient matrixes were carried out to ascertain the relationship between the pollutants concentration in the biota and sediments. Furthermore, predictive modeling of pollutant concentration in flesh and shell of *Tympanotomus fuscatus* was estimated. The results indicate that the amounts of HM, TPH and THC in some of the study sites were above the maximum permissible limit set by WHO and FMEnv; thus, pose health risk to humans.

Keywords: Pollution, heavy metals, total hydrocarbon content, total petroleum hydrocarbon, tympanotamus fuscatus, sediments, modelling

1.0 INTRODUCTION

The well-being and means of survival of human beings are dependent on their environment; hence there is need for environmental management best practices. The occurrence of crude oil in the Niger-Delta with its concomitant petroleum industrialization has resulted in the generation of enormous waste products, most of which are not efficiently disposed[1]. Some of the serious environmental problems that have arisen in the marine environment as a result of the activities of the upstream and downstream petroleum industries include, depletion of marine organisms, destruction of algae and some planktons as well as the interference with spawning areas on the seabed. Most of the pollutants generated by these petroleum activities are deposited on river sediments when discharged into the aquatic environment. Qua Iboe river, which is the research study area, is in the Niger Delta region of Nigeria where various oil and gas exploration and other petroleum related activities are rampant. Most of the effluents generated by these activities end up in the aquatic environment and are taken up by marine organisms. Periwinkle (*tympanotomus*

fuscatus), which is a major staple food in the region, resides in the sediments of the river and are sedentary or bottom feeders. They act as pollution biomonitors since they are good accumulators of heavy metals and hydrocarbon[1,2]. These pollutants are not biodegradable, accumulating over time in the sediments and marine organism; thereby pose severe consequences on the population that consume the polluted organism. Some of the human health hazards associated with these pollutants include damages to the lungs, liver, central nervous system, skin irritation while some of the pollutants have been classified as mutagenic, teratogenic and carcinogenic. Therefore, there is need for periodic environmental monitoring of aquatic bodies to ensure the well-being of flora and fauna that rely on the aquatic resources.

2.0 MATERIALS AND METHODS

2.1 Study Area

The Qua Iboe River is in Ibeno Local Government area of Akwa Ibom state. It is a major important hydrographic feature of the Niger Delta. The river is characterized by fine psammitic beaches, fringed with tidal mudflats and mangrove swamps. The river is located within latitude $4^{o}30^{'}$–$4^{o}45$'N and longitude $7^{o}30^{'}$ – $8^{o}45^{'}$E on the South-East Coastline of Nigeria (Edu *et al.,* 2012).

The lower reach of the river is located close to petrochemical effluent treatment and discharge plant of a major multinational oil exploration company. The sample site location is described in the table below;

Table 1: Sample Location, Geographical Coordinate and Site Description

Site code	Co-ordinate	Site Description
S 1	N04^{o} 34' 56.74" E07^{o} 54' 50.96"	**Nditia:** This site is located in the dredging area of the river. Petty trading, fishing and cattle rearing activities observed in this area. Discharge of sewage and household waste into the river, dumpsites and people bathing around the river bank is prevalence.
S 2	N04^{o} 34' 56.74" E07^{o} 54' 50.96"	**Ukpennekang:** This site experiences a lot of human activities such as welding, farming, trading, boat fabrication, lumbering work, washing of cars and clothing. There is also the presence of a local fish market.
S 3	N04^{o} 33' 04.3" E008^{o} 00' 01.2"	**Mkpanak:** A major multinational oil company and allied oil/gas servicing companies are situated in this area. The effluent treatment and discharge unit of the companies are also located in this area, as well as gas flaring. Human activities such as welding,

		fishing, farming and trading are prevalence.
S 4	N04^{o} 32' 49.8" E007^{o} 59' 21.0"	**Itak-Abasi:** This area is closest to the Atlantic Ocean. A lot of fishing activities, fabrication of engine boats take place here. Abandoned boats, used tyres and other waste were also noticeable in this site. This site also serves as the boat berthing point. Flourishing mangrove was seen all around.
S 5	N4^{o} 47' 0.50" E7^{o}52' 55.80"	**Ikot-Ibok:** This site is devoid of any human activity. It serves as the control site.

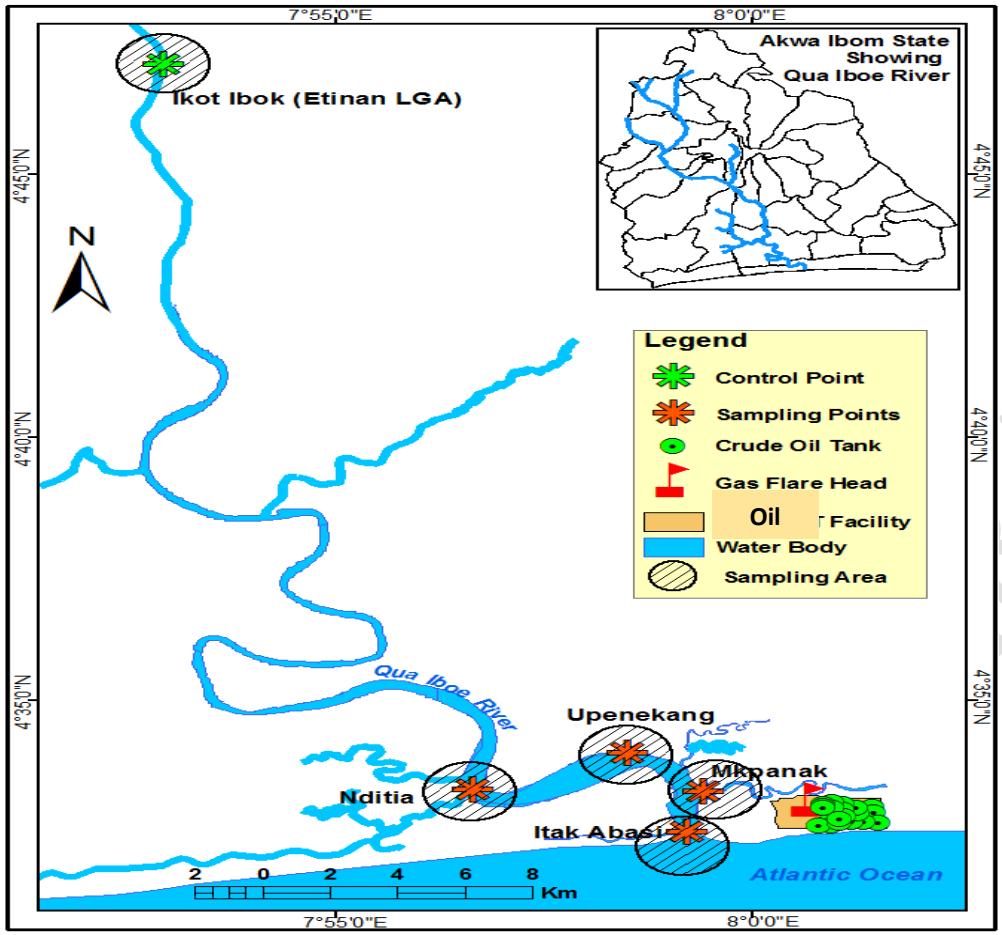

Fig. 2.1 Location of Sampling Points along Qua-Iboe River

2.2 Sample Collection and Treatment (Sampling)

2.2.1 *Tympanotomus Fuscatus* (Perewinkle)

The mature fresh samples of periwinkle, which are highly consumed in this region of the country, were collected in triplicate using Quadrat sampling method according to Clapcott et al[4]. A series of square (quadrants) were placed in the habitat of interest and the species of interest identified and collected. The samples were collected from five different sites along the river body namely; Nditia, Ukpenkang, Mkpanak, Itak-Abasi and Ikot-Ibok (the control site) during the dry. (December 2016, January – February, 2017) and wet (July, august September, 2017) seasons.

2.2.2 Sediments

The sediment samples were collected from the five study sites using a clean Van Veen grab sampler. The samples were placed in one-liter amber glass bottles and polythene bags previously acid washed as stated above. It was placed in an ice chest with ice for transportation to the laboratory and thereafter kept under refrigerator and protected from light until analysis to avoid photo degradation of the samples.

2.3 Determination of TPH and THC in *Tympanotomus Fuscatus*

Total Petroleum Hydrocarbon (TPH) and Total Hydrocarbon Content (THC) were determined using gas chromatography fitted with flame ionization Detector (GC-FID) as described by MERLL[5]. According to the procedure outlined by Schwab et al.[6], each of the fresh samples were cut into pieces using a stainless steel knife and then crushed with the help of a porcelain mortar and pestle. 10g of each of the crushed samples

were weighed into a 100ml beaker and 60ml of TPH extraction mixture was then added. The beaker with its content was placed on a magnetic stirrer (with heater) and shaken for about 15mins at 70^{o}C and the extract was decanted. 30ml of fresh extraction solvent was added and the process of shaking on the magnetic stirrer repeated. 5g of anhydrous Sodium Sulphate was used to remove water from the extract. The extract was concentrated to 3ml with rotary evaporator maintained at 20^{o}C.

1.5ml of the concentrated extract was loaded on a silica gel column and eluted with 30ml HPLC hexane into a well labeled 100ml beaker to get the aliphatic hydrocarbon components in the sample.

2.4 Determination of TPH and THC from Sediment

In the laboratory, sediment samples were dried at ambient temperature in open containers covered lightly with clean paper and then stored in clean bottles. The samples were ground with a porcelain mortar and then passed through a series of graduated strainers to remove stones and vegetable matter. 10g of the sample was weighed into a 100ml beaker and the above method for *Tympanotomus Fuscatus* extraction was repeated for sediment samples using acetone/dichloromethane mixture as extraction solvent[6].

2.5 Determination of Heavy Metals

The perewinkle and sediment samples were digested after drying at a temperature of 105^0C for 24hrs according to AOAC[7] methods. The levels of Pb, Cd, Se, Cr, Cu, Ni, Fe and Zn was determined using buck scientific model 210VGP (Variable Giant Pulse) atomic absorption spectrophotometer with different hollow cathode lamp at different wavelength. While Hg and As were determined using graphite furnace Atomic Absorption Spectrometry (Perkin Elmer Model 1100B equipped with an HGA – 700 graphite furnace, and deuterium background corrector) because of its higher sensitivity.

All reagent used were of analytical grade and deionized water was used in all preparation except otherwise stated. 10ml of ratio 10: 1 mixture of Nitric (HNO_3) and Perchloric ($HClO_4$) acid was used to digest the samples before AAS analysis was carried out.

2.6 Determination of Proximate Composition

Proximate composition includes moisture, crude protein, ether extract, crude fibre, ash, and nitrogen free extract. Moisture was determined by oven dehydration method at 105^oC up to the constant weight. Crude protein was determined by using Kjeldhal method, crude fat was determined by ether extraction method using Sohxlet apparatus. Crude fibre was determined by acid and alkali digestion method. Ash content was determined in muffle furnace at 500^oC for six (6) hours. For all these determinations powdered sample were used in triplicate in accordance with AOAC[7]. Nitrogen free extract (NFE) was calculated by difference.

3.0 RESULTS AND DISCUSSION

3.1 *Tympanotomus Fuscatus* (Periwinkle)

Table 2: Proximate Analysis of *Tympanotomus Fuscastus*

Sample	Moisture Content (%)	Ash (%)	Fat (%)	Crude Fibre (%)	Protein (%)	Carbohydrate (%)
Flesh	6.021	25.00	9.049	0.098	0.002	58.026
Shell	0.001	94.00	3.019	0.008	0.015	1.714

Table 3: Heavy metals concentration in *Tympanotomus fuscastus* flesh during dry and wet seasons

Metals	Dry Season					Wet Season				
	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
Pb	1.05	1.071	2.00	1.699	0.0017	1.037	1.358	1.401	1.39	0.0017
Cd	0.001	0.00	0.088	0.08	0.00	0.002	0.029	0.05	0.05	0.00
Cu	0.004	0.006	10.01	10.01	0.0003	0.002	3.339	0.011	3.343	0.001
Se	4.067	4.09	5.063	5.057	0.0003	3.721	4.406	5.059	5.043	0.0017
Zn	1.051	1.393	0.056	0.054	0.0003	0.035	0.043	0.055	0.052	0.0147

As	0.015	0.017	0.014	0.013	0.000	0.355	0.019	0.013	0.011	0.000
Cr	1.081	1.09	1.099	1.091	0.0003	3.055	1.085	1.091	1.083	0.001
Fe	9.013	9.021	9.045	9.038	0.0003	6.036	9.041	9.043	9.034	1.0189
Ni	0.697	0.08	1.028	1.023	0.0007	0.055	0.377	1.223	1.022	1.0283
Hg	0.053	0.06	0.700	0.693	0.000	0.04	0.221	0.698	0.392	0.001

Table 4: Heavy metals mean concentration in *Tympanotomus fuscastus* shell during dry and wet seasons

Metals	**Dry Season**					**Wet Season**				
	S1	**S2**	**S3**	**S4**	**S5**	**S1**	**S2**	**S3**	**S4**	**S5**
Pb	1.054	1.081	2.002	1.099	0.001	1.036	1.048	1.401	1.395	0.0017
Cd	0.001	0.001	0.086	0.067	0.000	0.008	0.001	0.072	0.056	0.000
Cu	0.031	0.039	3.347	10.01	0.002	0.012	0.011	0.013	0.011	0.0013
Se	2.737	3.064	4.022	4.053	0.002	2.364	3.036	4.739	5.053	0.0023
Zn	1.022	1.033	0.057	0.053	0.017	0.025	0.028	0.057	0.052	0.0150
As	0.033	0.035	0.016	0.031	0.000	0.017	0.019	0.016	0.013	0.000
Cr	1.698	2.001	2.002	1.075	0.003	1.685	2.001	1.099	1.092	0.0027

Fe	2.734	3.083	10.022	9.044	1.039	2.384	2.721	10.02	9.693	1.028
Ni	0.053	0.061	1.048	1.02	0.03	0.045	0.054	1.046	1.032	1.030
Hg	0.039	0.05	1.0033	0.082	0.003	0.037	0.044	1.003	0.692	0.0017

Proximate analysis results for *Tympanotomus fuscatus* flesh are indicated in table 2 as follows: Moisture content (6.021%), Ash (25%), Fat (9.049%), Crude fibre (0.098%), Protein (0.002%) and Carbohydrate (58.026%), while for *Tympanotomus fuscatus* shell: Moisture content (0.001%), Ash (94%), Fat (3.019%), Crude fibre (0.008%), Protein (0.015%) and Carbohydrate (1.714%). Results of the investigation of heavy metals *in Tympanotomus fuscatus* flesh and shell are indicated in tables 3 – 4 respectively. The presence of some toxic metals in the flesh of the sample took these sequence across the sites (1 – 5), during dry season Cu > Fe > Se > Pb > Zn > Cr > Ni > Hg > Cd > As while in wet season the metals took these pattern; Fe > Se > Cu > Pb > Ni > Cr > Zn > Hg > Cd > As. Most of the metals in *Tympanotomus fuscatus* shell in Site 3 and 4 during dry season were Cu (0.0023 – 10.0100mg/kg), Fe (1.0280 – 10.0223mg/kg) and Hg (0.002 – 1.0033mg/kg). The seasonal variation of the metals in the sample may be attributed to anthropogenic activities, increased adsorption due to reduced level of water body as well as runoffs and direction of river flow[8]. Mercury toxicity can occur after microbial degradation of Hg to dimethyl mercury. Human exposure to dimethyl mercury occurs through consumption of contaminated marine or aquatic foods. Gbaruko and Friday[9] reported that Hg affects the central nervous system and brain due to its ability to cross the blood brain barriers. This investigation had shown Qua-Iboe river is under Hg pollution threat which might be as a result of gas flaring, oil exploitation/exploration and from waste discharged by the operating oil company[10]. According to

WHO[11], the marine environment can be contaminated through the introduction of mercury containing products into the river such as batteries, measuring devices such as thermometers, electric switches and relays in equipment, lamps (including some type of bulb), dental amalgam (for dental filling) skin lightening products and other cosmetics as well as pharmaceuticals. Consequently, elemental and methyl mercury are toxic to the central and peripheral nervous systems. The inhalation of mercury vapour can produce harmful effect on the nervous digestive and immune systems, lungs and kidneys and may be fatal[11].

3.2 Sediment

Table 5: Heavy metals mean concentration in Sediment during dry and wet seasons

Metals	Dry Season					Wet Season				
	S1	**S2**	**S3**	**S4**	**S5**	**S1**	**S2**	**S3**	**S4**	**S5**
Pb	1.732	2.345	2.026	2.015	0.056	1.399	2.003	2.009	1.698	0.0527
Cd	0.052	0.065	0.068	0.0287	0.000	0.041	0.222	0.027	0.0267	0.000
Cu	0.017	3.378	10.02	10.016	0.002	1.036	1.339	10.02	0.018	0.0017
Se	1.410	2.004	3.027	2.0077	0.003	1.388	2.004	3.369	3.367	0.0023
Zn	5.706	6.039	8.038	8.024	0.023	5.688	6.015	8.035	6.397	0.089
As	0.003	0.004	0.021	0.0317	0.003	0.005	0.004	0.002	0.019	0.000

Cr	0.019	0.020	2.052	2.057	0.005	0.016	0.018	2.055	2.0533	0.061
Fe	52.724	62.70	73.691	62.701	1.052	49.11	60.35	86.69	27.351	1.0447
Ni	0.019	0.021	5.041	5.038	0.004	0.017	0.015	5.041	5.0397	0.0047
Hg	1.019	1.016	1.053	1.054	0.001	0.06	0.039	1.051	1.05	0.0017

Investigation of heavy metals in sediment (table 5) revealed a high availability of most of the metals under study, in the order: Fe > Cu > Zn > Ni > Se within both seasons. Fe gave the highest mean concentration during wet season, with a value of 86.6860mg/kg which is above WHO/FEPA (1.0mg/kg) permissible standard and control (1.0497mg/kg). The mean concentration of Fe within both seasons could be attributed to run-off during rainy season and anthropogenic activities, since sediment is a pollutant sink[12]. The soluble species of Fe reacts with sulphide in water to form yellow flocculants which could be toxic when picked up by sea food[13].

Eddy et al[14] in his study suggested that pollution of the environment by Fe cannot be conclusively linked to waste material alone but other natural sources of iron must be taken into consideration. Comparatively the concentration of iron in sediment in this study exceeded that of previous study by Moses et al.[15], where 27.04 $\pm$ 0.82 mg/kg was recorded at Ukpenekang (S1). The coefficient of variation (0.0115 – 74.5975%) showed that level of instability of Fe was higher in wet season than dry season.

The high presence of Zn in sediment with 0.230 to 8.038mg/kg and a coefficient of variation (C.V), 0.0249 – 127.4719% within both seasons may be attributed to various anthropogenic activities such as washing of motor and vehicles in various site at the bank of the river. It reported

that zinc is sourced from industries involved in smelting, electro-galvanizing, mining, metallurgy, production of pesticides, rubber plastics and various alloys[16]. Observed Zn concentrations in this study could still be attributed to activities of boat welders/ fabricators, decayed boat, waste containing fibres and papers, mixed effluent (dung's poultry droppings and fertilizer) including human and animal food where it is concentrated in excretions which get flushed into inland water bodies through flood run-off water. In terms of toxicity, an excess of Zn can be detrimental causing vomiting, abdominal pains, cramps, renal damage, hemorrhagic pancreation and fatality in humans[17]. From the foregoing, it has become very necessary to implement existing policies to check the unwarranted dumping of refuse and discharge of harmful substances into Qua-Iboe River (inland water bodies) to avert possible hazards.

The sediment also exhibited minimal concentration of Arsenic (As) within the mean concentration ranged of 0.0000 – 0.0203mg/kg and a C.V of 0.0000% to 193.3333%. The mean concentrations of Ni in the sample where slightly less than WHO (0.05mg/kg) but were within the FEPA (0.2mg/kg) standard. Arsenic levels recorded in wet season were slightly higher than in dry season. This may be due to run-off, tidal incursions and flooding. This corroborates with the research undertaken by Vaikosen *et al.*[18], who reported a higher value in wet season than the dry season. The finding in this study is consistent with the result of other studies[19,20]. Environmental pollution by arsenic may arise from agricultural practices (weed killer, fungicide, rodenticides and insecticides) and from industry. It has been confirmed that arsenic and arsenical compounds are found in waste waters of metallurgical industry, glassware, ceramic production, tannery operations, dye, herbicides and pesticides manufacture[21]. Other industrial sources include the organic chemicals and petroleum refining industries. Arsenic has serious effect on health and environment; inorganic arsenic can produce acute and chronic effect in the respiratory organs, gastrointestinal tract, skin, cardiovascular system,

nervous system and blood forming organs. Hence there is urgent need for remediation, routine monitoring and legislation on waste dumping into the river.

The concentration of Cu in sediment had a mean range of 0.0020 – 10.0193 mg/kg and 0.0017 – 10.0197mg/kg within dry and wet season respectively. The highest value was recorded during the wet season and may have resulted from run-off/wash-off due to the oil company operations. Comparatively most of the obtained values were above WHO (1.50mg/kg) and FEPA (0.1mg/kg) permissible standard for biota. This high concentration could have possibly been due to sedimentation from direct disposal of effluent rich in Cu[22]. Copper forms stable complexes with organic matter such that only a small fraction of this metal exists as free-hydrated ions especially when the sediment is slightly acidic. This justifies the low levels of Cu found in the river water with high amount of sediment.

3.3 Transfer factor

Transfer factor is the ratio between the accumulated concentration of a given pollutant in any organ and its dissolved concentration in water. It gives an indication about the accumulation efficiency for any particular pollutant in any fish organ. It can be calculated using the formular;

$$TF = \frac{M_{tissue}}{M_{water}} \qquad (3.1)$$

In general transfer factor explains the potentiality of heavy metals being absorbed by biota. According to Karazzaman et al.[23], the presence of metal in high level in fish environment does not indicate a direct toxic risk to fish, if there is no significant accumulation of metal by fish tissue.

Transfer factor (T.F) is a powerful tool for processing the bioaccumulation information for sediment and biota[24]. In agreement with this assertion, Olanescu[25] proposed an equation to relate the heavy metal transfer from sediment in biota thus;

$$TF = \frac{M_{biota}}{M_{sediment}} \quad (3.2)$$

Where TF is the Transfer factor

M_{biota} = Metal content in biota (flora or fauna)

$M_{sediment}$ =Metal content in sediment (mg/kg)

Table 6: Transfer factor for *Tympnotomus Fuscatus* flesh during dry and wet season

Metal	**S 1**		**S 2**		**S 3**		**S 4**		**S 5**	
(mg/kg)	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
Pb	0.6080	0.7408	0.4568	0.6779	0.9874	0.6976	0.8434	0.8201	0.0304	0.0323
Cd	0.0127	0.0564	0.0000	0.1338	1.2884	1.8630	2.7875	1.8240	0.0000	0.0000

Cu	0.2157	0.0016	0.0017	2.4929	0.9992	0.0011	2.9993	185.7056	0.6500	0.5882
Se	2.8835	2.67100	2.0414	2.1991	1.6723	1.5017	2.5190	1.4978	0.6970	0.7391
Zn	0.1841	0.0061	0.2307	0.0071	0.0069	0.0068	0.0068	0.0081	0.7957	0.1652
As	5.1110	66.5042	4.6757	5.2162	0.6908	0.6552	0.4196	0.5947	0.0000	0.0000
Cr	57.9275	194.9746	53.6946	61.3164	0.5355	0.5310	0.5302	0.5274	0.2600	1.000
Fe	0.1709	0.1229	0.1439	0.1498	0.1227	0.1043	0.1441	0.3303	0.9806	0.9707
Ni	3.6667	3.2549	3.7952	2.5083	0.2035	0.2427	0.2031	0.2027	0.4595	218.7872
Hg	0.0527	0.6722	0.0593	0.5603	0.6651	0.6644	0.6575	0.3736	2.3077	0.5882

The transfer factor (table 6) has appropriately assessed the biota and sediment during dry and wet season; most of the metals have shown a transfer factor greater than 1 in samples, which calls for concern. These results show a high bioaccumulation of the metals in *Tympnatomus fuscatus* from sediment. These observations correlate with the investigations of Gene and Yilmaz[24] on the levels of heavy metal in water, sediment and fish from lagoon system. In this study, the transfer factor is generally higher in wet season than in dry season (with few exceptions) and the trend for heavy metals was as follows; Cr > As > Ni > Se > Pb > Cu > Hg > Cd. Also, the result in this study implies that sediment to

biota transfer of heavy metals is a major pathway of human exposure to sediment contamination, as such the high transfer factor from sediment to biota indicate a strong accumulation of the particular metals by biota. *Tympnatomus fuscatus* are found in sediments of the river and thus, are bottom feeders; they take up heavy metals from the sediments, especially during feeding, accumulating them in their tissues over time. Consumption of these contaminated organisms by humans poses a serious health risk to the consumers.

3.4: The Multiple Correlation Coefficient Matrixes: Tables A1 – A4 were calculated and defined based on the Hatva's Scale, in order to ascertain the relationship between the metals in sediment and biota. The coefficient measures the strength of a linear relationship between any two variables on a scale of – 1 (perfect inverse relation) through 0 (no relation) to + 1 (perfect sympathetic relation)[26].

3.4.1 Correlation of *Tympanotomus fuscatus* flesh: Tables A1 & A2 show the result of sediment and *Tympanotomus fuscatus* correlation coefficient during dry and wet season. During dry season, a very strong association (r = 0.998-0.999) was observed among the following metals, Cr/Cr, Cu/Ni, Se/Zn, Cr/Hg, Fe/Hg Ni/Cr, Hg/Cr and Hg/Ni. There was also strong association among, Pb/Cu, Pb/Se, Cd/Cu, As/Fe, Cr/Pb, Ni/Cu, Hg/Cu and Ni/As. Moderate (r = - 0.7- 0.31) negative relationship existed between Zn/As, Zn/Cr and Zn/Ni which implies that they do not have the same sources of enrichment. However, during wet season, Pb/Hg, Cr/Hg and Fe/Hg exhibited a very strong positive relationship. Hg correlated well with all the elements which further confirmed its common source of association as a result of introduction of mercury containing products such as batteries, thermometers, electrical appliances and pharmaceutical product into the river[11]. Mercury toxicity can occur after microbial degradation of Hg to dimethyl mercury. Human exposure to dimethyl mercury occurs through consumption of contaminated marine or aquatic foods. Hg affects the central nervous system and brains due to its ability to cross the blood brain barriers[9].

3.4.2: Correlation of *Tympanotomus fuscatus* shell: Tables A3 & A4 show the results of sediment – biota (*Tympanotomus fuscatus* shell) during dry and wet season. It was observed that a very strong positive significant correlation (r= 0.993 - 0.999) occurred between Se/Zn, Cr/Cd, Ni/Cr and Ni/Ni during dry season while in wet season a similar trend occurred between Pb/Zn, Cu/Fe, Zn/Cu and Fe/Cu. Strong positive significant correlation was recorded among Pb/Se, Ni/Cu and Pb/Fe, Fe/Cr in dry and wet season respectively. Many other relationships between various quantitative variables are also significant with least values[27]. The above result is an indication that *Tympanotomus fuscatus* shell derived its pollutant from the sediment which might be as a result of run-off and anthropogenic activities, especially Ni which correlates strongly with the other metals and could originate from plating and printing materials being dumped into the river overtime. Finally, the result agrees with a research by Rakesh and Raju[28] on correlation of heavy metal contamination with soil properties of industrial areas.

3.5: Concentration (m/kg) of TPH AND THC in Sediment and *Tympanotomus fuscatus* during dry and wet season.

Table 7: Concentration (mg/kg) of the TPH and THC in *Tympanotomus fuscatus* and sediments during dry and wet season

Site	Sample	TPH		THC	
		Dry Season	Wet Season	Dry Season	Wet Season
S1	*T. fuscatus* flesh	237.556	160.86	921.28	728.47
	T. fuscatus shell	758.1367	584.60	1134.98	783.067
	Sediment	246.513	175.97	579.58	492.41
S 2	*T. fuscatus* flesh	263.153	177.673	964.937	773.87
	T. fuscatus shell	843.696	632.65	1218.627	910.58
	Sediment	263.713	186.327	631.883	536.667
S 3	*T. fuscatus* flesh	646.883	577.993	1707.29	1187.26
	T. fuscatus shell	1081.5167	937.233	2442.04	1809.44
	Sediment	3143.91	2763.51	7186.25	6868.607
S 4	*T. fuscatus* flesh	530.113	256.85	1337.02	964.09
	T. fuscatus shell	978.64	466.193	1799.91	1292.803
	Sediment	3122.92	1443.6	9859.95	1761.05

S 5	*T. fuscatus* flesh	73.91	46.63	849.943	727.6167
	T. fuscatus shell	54.24	29.393	158.83	135.343
	Sediment	607.803	504.457	855.377	813.740

TPH and THC were investigated in *Tympanotomus fuscatus* and sediment in four sites namely S1 (Nditia), S2 (Ukpenekang), S3 (Mkpanak), S4 (Itak-Abasi) and S5 (control at Ikot-Ibok). General observations after the analysis were that; THC in all the samples under study was higher than TPH. Moreso, S3 had the highest concentration of TPH and THC this could be linked to oil spillage from oil facility of operating oil company overtime as well as other anthropogenic activities that may introduce gasoline, alkanes water soluble aromatics (BTEX, substituted benzene) and water insoluble polyaromatic hydrocarbon[29]. The least concentrations were recorded in S1 (Nditia) and S2 (Ukpenekang). This was due to less human activities, and the direction of river flow was from less polluted area. Extractable petroleum hydrocarbons in this study contains C_9 to C_{30}, constituting more of jet propellant (JP – 5, JP – 7 and JP – 8) with some dearomatised petroleum stream and mineral oil which is a mixture of naptha, gasoline, and kerosene hydrocarbon[29]. TPH/THC control samples were lower than values obtained from all locations and above the regulatory limits of 0.6mg/kg by DPR[30]. However, TPH/THC compounds have been reported[31] to be of detrimental effect to human, by affecting central nervous system, headaches, dizziness at high concentrations, effect on the blood, lungs, skin and eyes.

3.6: Predictive modelling of Heavy metals, TPH and THC in Qua-Iboe river basin.

Table 8: Comparison of different regression models predicting heavy metals concentrations of the flesh of *Tympanotomus fuscatus* from the shell concentration.

Linear			Power			Exponential		
Equation	R^2	p	Equation	R^2	P	Equation	R^2	P
$Pb_{flesh} = 0.03 + 1.00Pb_{shell}$	0.910	0.000	$Pb_{flesh} = 1.02(Pb_{shell})^{1.00}$	0.998	0.000	$Pb_{flesh} = 0.01e^{3.61Pb_{shell}}$	0.719	0.000
$Cd_{flesh} = 0.001 + 0.90Cd_{shell}$	0.743	0.000	$Cd_{flesh} = 0.46(Cd_{shell})^{0.81}$	0.807	0.000	$Cd_{flesh} = 0.002e^{47.14Cd_{shell}}$	0.846	0.000
$Cu_{flesh} = 0.39 + 0.96Cu_{shell}$	0.800	0.000	$Cu_{flesh} = 0.65(Cu_{shell})^{0.98}$	0.766	0.000	$Cu_{flesh} = 0.004e^{0.77Cu_{shell}}$	0.754	0.000
$Se_{flesh} = 0.54 + 1.06Se_{shell}$	0.902	0.000	$Se_{flesh} = 1.17(Se_{shell})^{1.07}$	0.995	0.000	$Se_{flesh} = 0.008e^{1.64Se_{shell}}$	0.767	0.000
$Zn_{flesh} = -0.002 + 1.18Zn_{shell}$	0.980	0.000	$Zn_{flesh} = 0.58(Zn_{shell})^{0.76}$	0.768	0.000	$Zn_{flesh} = 0.03e^{1.54Zn_{shell}}$	0.875	0.000
$As_{flesh} = 0.009 + 2.20As_{shell}$	0.071	0.209	$As_{flesh} = 1.00(As_{shell})^{1.02}$	0.715	0.000	$As_{flesh} = 0.005e^{38.96As_{shell}}$	0.487	0.000
$Cr_{flesh} = 0.62 + 0.35Cr_{shell}$	0.038	0.301	$Cr_{flesh} = 0.67(Cr_{shell})^{1.04}$	0.926	0.000	$Cr_{flesh} = 0.007e^{2.92Cr_{shell}}$	0.616	0.000
$Fe_{flesh} = 4.39 + 0.54Fe_{shell}$	0.344	0.001	$Fe_{flesh} = 1.52(Fe_{shell})^{0.89}$	0.377	0.000	$Fe_{flesh} = 2.03e^{0.17Fe_{shell}}$	0.256	0.004

$Ni_{flesh} = 0.009 + 1.02Ni_{shell}$	0.957	0.000	$Ni_{flesh} = 1.11(Ni_{shell})^{1.05}$	0.971	0.000	$Ni_{flesh} = 0.032e^{3.30Ni_{shell}}$	0.792	0.000

Table 9 Comparison of different regression models predicting THC of the shell and flesh of *Tympanotomus fuscatus* from TPH.

Linear			**Power**			**Exponential**		
Equation	**R^2**	**P**	**Equation**	**R^2**	**P**	**Equation**	**R^2**	**P**
$THC_{shell} = 8.62 + 1.88TPH_{shell}$	0.909	0.000	$THC_{shell} = 8.87(TPH_{shell})^{0.76}$	0.968	0.000	$THC_{shell} = 133.00e^{0.003TPH_{shell}}$	0.989	0.000
$THC_{flesh} = 663.15 + 1.28TPH_{flesh}$	0.832	0.000	$THC_{flesh} = 292.94(TPH_{flesh})^{0.23}$	0.701	0.000	$THC_{flesh} = 716.690e^{0.001TPH_{flesh}}$	0.846	0.000

The application of different models (tables 8 & 9) such as bivariate linear regression, power equation and exponential equation technique enable predictive equations to be derived as illustrative models, based on the responses of concentration of contaminant in flesh as function of shell totals. It also identified relative abundance of accumulation of contaminants in both tissues (flesh) and shell of *Tympanotomus fuscatus*. The most valuable contribution of these is not in predicting presence of contaminant as such, but also in creating awareness on the deleterious effect of these pollutants to man[32]. The applicability of regression techniques in the prediction of contaminants concentration in tissues and organs of aquatic biota is well established in in literature[33]. This applicability stems from the fact that regression techniques derive a relationship between

pairs of variables, in that it predicts the value of one (dependent) from the other (predictor)[34], as evident in this study. The prediction of hydrocarbons (TPH & THC) and heavy metals concentrations in the flesh of *Tympanotomus fuscatus* from its shell concentration at highly significant statistical level (p-value ≤ 0.05) are shown in tables 8 & 9. It indicates that the shell concentration is a good indicator of concentration of these pollutants in the flesh.

According to the models in table 8, it is observed that the power model best predicts the relationship between Pb, Se, As, Cr, Fe, and Ni in the shell in comparison with the flesh while the linear model best predict the relationship between the relationship between Cu and Zn in the shell in comparison with the flesh. Exponential model best predicts the relationship between the Cd in the shell with the Cd in the flesh of *Tympanotomus fuscatus*.

Table 9 shows that exponential model best predicts the THC of the shell and flesh of *Tympanotomus fuscatus* from TPH based on the coefficient of determination (R^2) value of 0.989 and 0.846 for shell and flesh respectively.

4.0 CONCLUSION

This research was carried out to assess the concentration of heavy metals, TPH and THC in sediment and *Tympanotomus fuscatus* obtained from Qua Iboe River and its environs. Also, heavy metals bioaccumulation was estimated using transfer factor**.** Generally, HM, THC and TPH

concentrations in the river were higher in dry season than wet season. The results indicate that the amounts of HM, TPH and THC in some of the study sites were above the maximum permissible limit set by WHO and FMEnv; thus, pose health risk to humans. This study has created awareness, as well as provides baseline information on the distribution assessment of TPH, THC and heavy metals, highlighting the impact of petroleum, hydrocarbon and heavy metals pollutants on aquatic environment.

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APPENDICES

Table A1: Sediment-biota (*Tympanotomus fuscatus flesh*) Dry season correlation matrix

	SedPb	SedCd	SedCu	SedSe	SedZn	SedAs	SedCr	SedFe	SedNi	SedHg	TyFlPb	TyFlCd	TyFlCu	TyFlSe	TyFlZn	TyFlAs	TyFlCr	TyFlFe	TyFlNi	TyFlHg
SedPb	1																			
SedCd	.861	1																		
SedCu	.680	.500	1																	
SedSe	.889	.888	.841	1																
SedZn	.922	.748	.911	.944	1															
SedAs	.511	.195	.937	.615	.782	1														
SedCr	.457	.288	.963*	.693	.765	.949	1													
SedFe	.966*	.871	.819	.973*	.976*	.631	.638	1												
SedNi	.454	.287	.962*	.692	.763	.948	1.000**	.636	1											
SedHg	.984*	.824	.801	.931	.977*	.648	.609	.990*	.606	1										
TymFlPb	.829	.718	.961*	.957*	.974*	.818	.861	.939	.860	.912	1									

TymFlCd	.451	.318	.959*	.711	.760	.925	.998**	.642	.998**	.603	.866	1								
TymFlCu	.452	.285	.961*	.690	.762	.948	1.000**	.634	1.000**	.605	.858	.998**	1							
TymFlSe	.944	.773	.884	.945	.998**	.749	.725	.985*	.723	.988*	.961*	.720	.722	1						
TymFlZn	.490	.522	-.306	.152	.115	-.449	-.552	.280	-.554	.326	-.067	-.555	-.556	.174	1					
TymFlAs	.996**	.890	.626	.878	.892	.438	.392	.953*	.390	.967*	.795	.390	.388	.917	.549	1				
TymFlCr	.989*	.835	.783	.928	.970*	.625	.585	.989*	.583	1.000**	.901	.580	.581	.983*	.353	.975*	1			
TymFlFe	.989*	.833	.781	.926	.969*	.626	.584	.988*	.581	1.000**	.900	.578	.580	.982*	.355	.975*	.999**	1		
TymFlNi	.501	.331	.975*	.726	.797	.951*	.999**	.676	.999**	.648	.885	.996**	.998**	.759	-.509	.438	.625	.624	1	
TymFlHg	.506	.338	.976*	.731	.800	.949	.998**	.680	.998**	.652	.888	.996**	.998**	.762	-.505	.443	.629	.628	.999**	1

Table A2: Sediment-biota (*Tympanotomus fuscatus flesh*) Wet season correlation matrix

	SedPb	SedCd	SedCu	SedSe	SedZn	SedAs	SedCr	SedFe	SedNi	SedHg	TymFlPb	TymFlCd	TymFlCu	TymFlSe	TymFlZn	TymFlAs	TymFlCr	TymFlFe	TymFlNi	TymlHg
SedPb	1																			
SedCd	.509	1																		
SedCu	.476	-.145	1																	
SedSe	.873	.047	.505	1																
SedZn	.970*	.287	.602	.951*	1															
SedAs	.633	-.339	.574	.922	.794	1														
SedCr	.514	-.467	.521	.861	.696	.989*	1													
SedFe	.843	.379	.831	.680	.855	.528	.410	1												
SedNi	.526	-.454	.523	.869	.706	.991**	1.000**	.419	1											
SedHg	.747	-.176	.531	.975*	.874	.984*	.952*	.587	.957*	1										
TymFlPb	.986*	.423	.407	.925	.973*	.708	.603	.764	.615	.818	1									
TymFlCd	.879	.053	.527	1.000**	.957*	.921	.858	.700	.865	.973*	.927	1								
TymFlCu	.507	.622	-.517	.365	.358	.069	.006	.001	.017	.221	.564	.349	1							
TymFlSe	.971*	.332	.437	.958*	.981*	.774	.679	.752	.690	.870	.995**	.959*	.522	1						
TymFlZn	.937	.186	.532	.988*	.986*	.861	.780	.763	.789	.932	.967*	.990**	.398	.987*	1					

TymFlAs	.941	.771	.295	.664	.830	.334	.195	.773	.210	.483	.896	.671	.620	.849	.766	1			
TymFlCr	.989*	.446	.398	.915	.969*	.690	.583	.766	.595	.803	1.000**	.917	.574	.992**	.961*	.907	1		
TymFlFe	.988*	.447	.394	.915	.968*	.689	.582	.762	.594	.802	1.000**	.917	.579	.992**	.960*	.907	1.000**	1	
TymFlNi	-.248	-.945	.449	.194	-.004	.556	.653	-.055	.642	.401	-.183	.194	-.666	-.088	.073	-.556	-.206	-.209	1
TymFlHg	.751	-.133	.838	.888	.884	.908	.854	.818	.858	.905	.757	.899	-.082	.802	.882	.503	.745	.742	.434	1

Table A3: Sediment-biota (*Tympanotomus fuscatus shell*) Dry season correlation matrix

	SedPb	SedCd	SedCu	SedSe	SedZn	SedAs	SedCr	SedFe	SedNi	SedHg	TyShPb	TyShCd	TyShCu	TyShSe	TyShZn	TyShAs	TyShCr	TyShFe	TyShNi	TyShHg
SedPb	1																			
SedCd	.861	1																		
SedCu	.680	.500	1																	
SedSe	.889	.888	.841	1																
SedZn	.922	.748	.911	.944	1															
SedAs	.511	.195	.937	.615	.782	1														
SedCr	.457	.288	.963*	.693	.765	.949	1													
SedFe	.966*	.871	.819	.973*	.976*	.631	.638	1												
SedNi	.454	.287	.962*	.692	.763	.948	.999**	.636	1											
SedHg	.984*	.824	.801	.931	.977*	.648	.609	.990*	.606	1										
TyShPb	.804	.868	.833	.987*	.892	.588	.714	.923	.714	.859	1									
TyShCd	.452	.369	.950	.739	.755	.884	.986*	.653	.986*	.601	.781	1								
TyShCu	.369	-.053	.785	.376	.623	.950	.817	.442	.816	.496	.323	.709	1							
TyShSe	.925	.748	.907	.942	1.000**	.781	.760	.977*	.758	.978*	.888	.749	.623	1						
TyShZn	.499	.531	-.296	.163	.125	-.441	-.543	.290	-.546	.335	.062	-.534	-.446	.133	1					
TyShAs	.900	.605	.471	.610	.756	.424	.240	.776	.237	.853	.474	.173	.417	.763	.617	1				
TyShCr	.914	.993**	.550	.909	.805	.268	.330	.913	.328	.880	.873	.393	.039	.805	.541	.688	1			
TyShFe	.611	.479	.992**	.826	.867	.917	.979*	.776	.978*	.742	.839	.980*	.746	.863	-.377	.363	.517	1		
TyShNi	.488	.328	.972*	.722	.787	.945	.999**	.667	.999**	.636	.742	.989*	.804	.782	-.513	.263	.368	.986*	1	
TyShHg	.317	.596	.608	.709	.498	.355	.621	.528	.623	.404	.815	.744	.057	.489	-.308	-.124	.544	.686	.639	1

Table A4: Sediment-biota *(Tympanotomus fuscatus shell)* Wet season correlation matrix

	SedPb	SedCd	SedCu	SedSe	SedZn	SedAs	SedCr	SedFe	SedNi	SedHg	TymShPb	TymShCd	TymShCu	TymShSe	TymShZn	TymShAs	TymShCr	TymShFe	TymShNi	TymShHg
SedPb	1																			
SedCd	.509	1																		
SedCu	.476	-.145	1																	
SedSe	.873	.047	.505	1																
SedZn	.970*	.287	.602	.951*	1															
SedAs	.633	-.339	.574	.922	.794	1														
SedCr	.514	-.467	.521	.861	.696	.989*	1													
SedFe	.843	.379	.831	.680	.855	.528	.410	1												
SedNi	.526	-.454	.523	.869	.706	.991**	.999**	.419	1											
SedHg	.747	-.176	.531	.975*	.874	.984*	.952*	.587	.957*	1										
TymShPb	.938	.210	.473	.987*	.978*	.848	.767	.730	.776	.926	1									
TymShCd	.531	-.458	.661	.849	.720	.983*	.985*	.517	.985*	.938	.757	1								
TymShCu	.986*	.360	.550	.936	.996**	.751	.645	.846	.657	.843	.976*	.664	1							
TymShSe	.876	.074	.452	.998**	.945	.908	.846	.652	.854	.967*	.989*	.824	.934	1						
TymShZn	.728	-.217	.616	.959*	.868	.991**	.960*	.627	.964*	.994**	.904	.963*	.831	.945	1					
TymShAs	.986*	.645	.393	.784	.916	.496	.366	.821	.379	.630	.874	.383	.945	.793	.604	1				
TymShCr	.882	.848	.150	.569	.741	.210	.072	.674	.087	.372	.696	.073	.793	.590	.330	.947	1			
TymShFe	.633	-.336	.555	.924	.792	.999**	.989*	.515	.991**	.986*	.850	.979*	.750	.911	.990*	.497	.213	1		
TymShNi	-.391	-.991**	.222	.084	-.159	.460	.579	-.280	.567	.303	-.079	.571	-.234	.057	.344	-.539	-.771	.457	1	
TymShHg	.556	-.425	.725	.847	.742	.972*	.966*	.581	.966*	.929	.760	.996**	.685	.818	.961*	.411	.099	.967*	.539	1

**. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).