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Heavy Metal Concentrations in Two Anadromous Fishes of Benin River in Relation to Human Health through Consumption.

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Abstract
Human health risk assessment of heavy metal contamination through consumption of two fish species namely Pomadasys peroteti and Albula vulpes from Benin River, in Koko Town (Southern Nigeria) was studied. Assessment of heavy metal concentrations was conducted in the liver, kidney and muscles of the fishes using Atomic Absorption Spectrophotometer. Mean heavy metal concentrations for Zn, Cd, Pb, Mn, As and Ni in P. peroteti were 2.65, 0.78, 0.15, 0.59, 0.49 and 0.86mg/kg for liver, 1.10, 0.32, 0.06, 0.25, 0.20 and 0.36mg/kg for muscle, 2.33, 0.68, 0.13, 0.52, 0.43 and 0.76mg/kg for kidney, respectively. In A. vulpes, concentrations were 0.69, 0.20, 0.04, 0.16, 0.13 and 0.23mg/kg for liver, 0.29, 0.08, 0.02, 0.06, 0.05 and 0.09mg/kg for muscle, 0.61, 0.18, 0.03, 0.14, 0.11 and 0.20mg/kg for kidney respectively. Target hazard quotients (THQs) for Cd, Pb, As, Ni, Mn and Zn were 0.0411, 0.0021, 0.0476, 0.0023, 0.0002 and 0.0005 for P. peroteti; 0.0010, 0.0007, 0.0214, 0.0006, 0.0001 and 0.0001 for A. vulpes. The highest THQ values were for Arsenic with the values 0.0476 and 0.0214 for P. peroteti and A. vulpes respectively. The least THQ values were for Mn with values 0.0002 and 0.0001 for P. peroteti and A. vulpes respectively. Arsenic was the major risk contributor while Mn was the least for both fish species studied. The total THQ (TTHQ) of P. peroteti and A. vulpes were 0.0938 and 0.0239 respectively. TTHQ in both fish species less than 1, suggesting that the consumption of P. peroteti and A. vulpes are unlikely to cause any adverse health effects to consumers.

Introduction
Heavy metals are considered one of the most important pollutants of the aquatic environment because of their toxicity and accumulation by aquatic fauna [1]. Heavy metals have accumulated in aquatic systems in the Niger Delta and this has become a source of concern to residents in affected localities [2]. The discharge of industrial wastes containing toxic heavy metals into water bodies may have significant effects on fish and other aquatic organisms, which may endanger public health through consumption of contaminated seafood. Aquatic organisms accumulate metals to concentrations many times higher than present in water or sediment and can take up metals concentrated at different levels in their different body organs [3]. Apart from destabilizing the ecosystem, the accumulation of toxic metals in aquatic food is a potential threat to public health. Heavy metals accumulate in the tissues of aquatic animals and may become toxic when accumulation reaches a substantially high level [4]. They pose a serious threat to human health, living organisms and natural ecosystems because of their toxicity, persistence and bioaccumulation characteristics [5]. Fish are known to be the living organisms most sensitive to trace concentrations of toxicants in the aquatic habitats [6]. Currently, fish is considered one of the most important foods to humans and is used in a variety of diets. It is a good source of digestible protein, vitamins, minerals, and polyunsaturated fatty acids. Heavy metals enter the fish through five main routes: via food or non-food particles, gills, oral consumption of water and skin.
In Nigeria, most studies on heavy metal pollution have concentrated on the levels of occurrence and distribution of these pollutants in sediment and surface water of aquatic resources [7] without relating the observed occurrence to biological effects on resident biota. Hazards associated with the consumption of heavy metals and their concentration in commercial fishes should be periodically examined to evaluate the possible risks associated with the consumption of contaminated fish. The Benin River (Koko Town) is situated in the north central part of Delta State. It drains the Ethiope, Ossiamo, Osse and Siluko into Atlantic Ocean.
This study is conducted to determine the levels of contamination and the concentration of Cadmium, Nickel, Manganese, Zinc, Arsenic and Lead in two common and edible fishes (*P. peroteti* and *A. vulpes*) that are found in Benin River. These fish species are of high commercial importance in Southern Nigeria.

Materials and Methods
Study area: The study area, Benin River (Koko Town) is situated in the north central part of Delta State between latitudes and longitude (N05^{0}54'14.9", E005^{0}41'50.7" – N05^{0}59'54.9", E005^{0}27'006") respectively. This River drains

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the Ethiope, Ossiamo, Osse and Siluko into Atlantic Ocean. Three distinct longitudinal zones could be recognized in this river, the upper freshwater zone, the middle transitional zone with salinity fluctuations and the lower coastal zone which is predominately saline. The present study was conducted in its upper fresh water reaches in commercial town of Koko. Fish was collected from a point located at the sampling point (Plate 1). Anthropogenic activities around this zone of the river include loading and offloading of petroleum products, bathing, fishing etc.

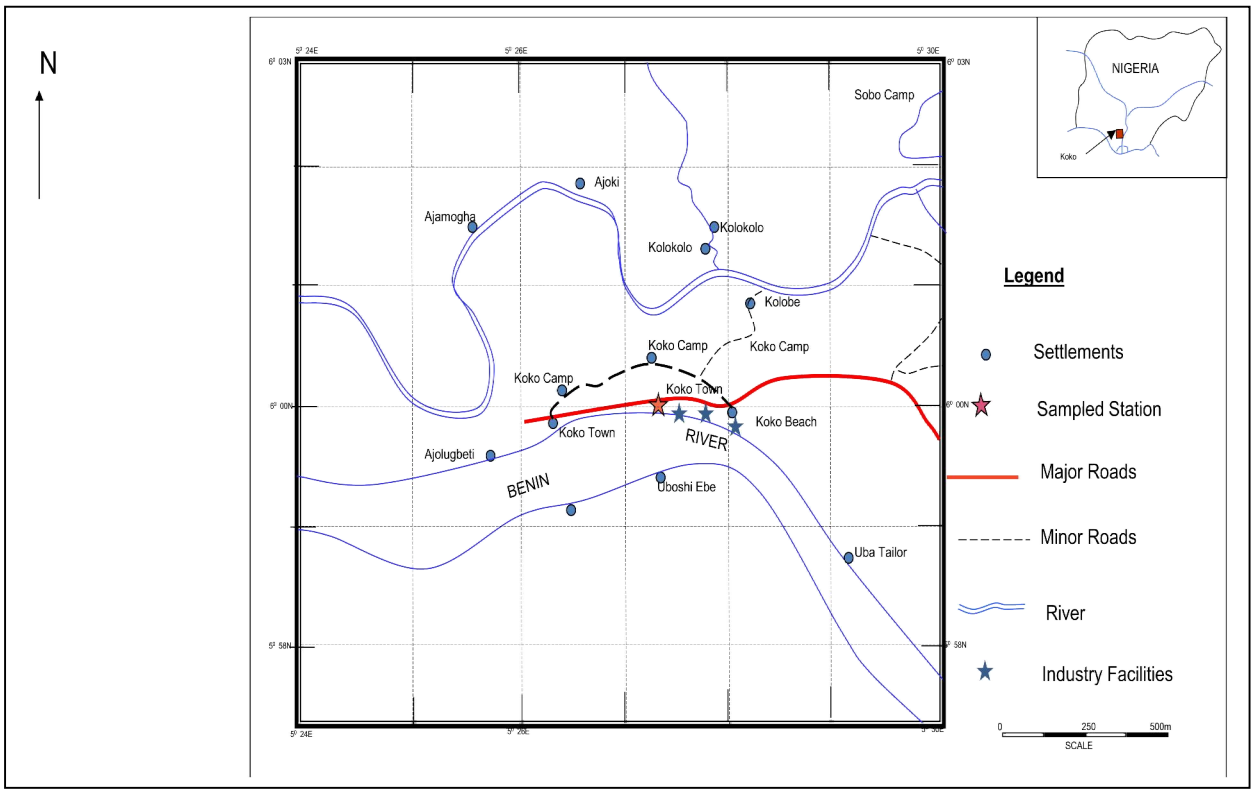

Plate 1: Study station

Fish identification and Sampling periodicity: The collection of fish samples from the river was done over a period of three months. During the entire study, three field trips were undertaken and three sets of fish sample were taken from each station. Fish were caught with gill nets, and local traps by the fishermen. The gill nets were set between 4.00pm and inspected the following morning at 6.00am, the fish samples were preserved in ice and taken to the laboratory. They were kept frozen in the refrigerator pending heavy metals analysis in the laboratory.

Plate 2: *Albula vulpes* from Benin River (Koko Town), Delta state, Nigeria

Plate 3: *Pomadasys peroteti* from Benin River (Koko Town), Delta state, Nigeria

Morphometric Measurement of fish: Total length (cm) of each fish was taken from the tip of the snout (mouth closed) to the extended tip of the caudal fin using a meter rule.

Sample preparation and metal analysis: In the laboratory prior to drying in an oven at 105℃, weights of *Albula vulpes* and *Pomadasys peroteti* samples were measured with the aid of electronic balance. Two grams of dried homogenised sample of each tissue was digested in 15 ml hydrochloric acid, 5mlnitric acid, and 5ml perchloric acid (3:1:1) solution and heated in a digester until brown fumes were expelled, tissues dissolved completely and a colourless solution obtained. The flask and its contents were allowed to cool and thereafter the digested sample was made up to 50ml with distilled water [8]. Fish samples were analysed for Zn, Cd, As, Pb, Mn and Ni using Atomic Absorption Spectrometry PG 550.

Quality Control Analysis: The equipment (AAS) was first calibrated using certified reference standard (SRM 1570) of the National Institute of Standards and Technology for the respective heavy metals to obtain calibration curve with the equation R^2 = 99.7. Reagent blank was run at intervals of every five samples analysis to eliminate equipment drift. All samples were analyzed in duplicates for reproducibility accurate checks and precision.

Target Hazard Quotient: The method for the determination of THQ was provided in the United States EPA Region III Risk based concentration table [9]. The dose calculations were carried out using standard assumptions from an integrated United States EPA risk analysis.

Assumptions for the health risk calculations are;

1. Ingested dose is equal to the absorbed pollutant dose [9].
2. Cooking has no effect on the pollutants [10].
3. The average body weight of a Nigerian is assumed to be 70 kg
4. Average lifetime of a Nigerian is 52 years.

THQ is determined by the following equation: $THQ = \frac{EFr \ x \ ED_{tot} \ x \ FIR \ x \ C}{RfDo \ x \ BWa \ x \ ATn} \ x \ 10^{-3}$

Where;

EFr is exposure frequency (365 days/year);
EDtot is the exposure duration 52 years, average lifetime);
FIR is the food ingestion rate (9kg/day);
C is the heavy metal concentration in *A. vulpes* and *P. peroteti* (mg/kg);
RfDo is the oral reference dose (mg/kg/day).
BWa is the average adult body weight (70 kg), and
ATn is the averaging exposure time for non carcinogens (365 days/year × number of exposure years assuming 52 years).

Since exposure to two or more pollutants may result in additive and/or interactive effects, total THQ in this study is treated as the arithmetic sum of the individual metal THQ values, derived by the method of Chien *et al*. [11].

Statistical Analysis*:* Metal concentrations are presented as mean ± standard error. Basic statistical measurement of central tendency and dispersion were carried out. The test for the significant differences in the heavy metals concentration were done with parametric analysis of variance (ANOVA) using the computer SPSS 16.0 windows application. Statistical significance was considered at ($P<0.05$).

Results

The summary of results of heavy metals concentrations in fishes Liver, muscle and kidney of A. *vulpes* and *P. peroteti* are presented in Figures 1 and 2. Figure 1 shows the concentration of the six heavy metals (Cd, Zn, Pb, As, Mn, and Ni) in *Albula vulpes*. Zn levels were highest with ranges between 0.49-0.92mg/kg in liver, followed by Mn levels with values ranging between 0.11 - 0.21mg/kg in the liver, then Nickel with values 0.16 - 0.30mg/kg. Next is Cd with mean levels ranged between a 0.14 - 0.27mg/kg in the liver. Arsenic have values between 0.09-0.17mg/kg in liver, and Pb with values ranged between 0.03 - 0.05mg/kg. it follows the same trend for other tissues. The values of the various metals were significantly different ($P<0.05$) among the fish tissues. The mean levels profile for the metals in *Albula vulpes* was Zn > Mn > Ni > Cd > As > Pb, the same profile was observed in all the tissues.

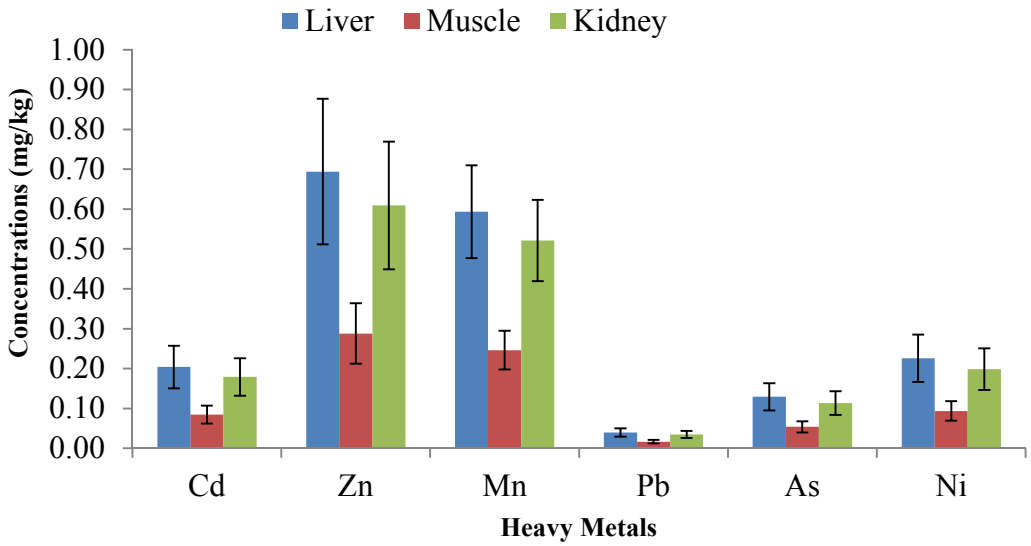

Figure 1: Mean levels of six heavy metals in *Albula vulpes*

Fig. 2 below shows the concentration of the six heavy metals (Cd, Zn, Pb, As, Mn, and Ni) in *P. peroteti*. Zn levels were highest in all tissues with values 1.86-3.51mg/kg (liver), 1.63-3.08mg/kg (Kidney), and 0.77-1.46mg/kg (muscle). Mn levels with values 0.42-0.79mg/kg (liver), 0.37-0.69mg/kg (kidney), and 0.17-0.33mg/kg (muscle). Nickel with values 0.60-1.14mg/kg (liver), 0.53-1.00mg/kg (kidney) and 0.25-0.47mg/kg (muscle). Cd levels ranged between 0.55-1.03mg/kg (liver), 0.48-0.91mg/kg (kidney), and 0.23-0.43mg/kg (muscle) Arsenic have values between 0.35-0.65mg/kg (liver) 0.30-0.57mg/kg (kidney) and 0.14-0.27mg/kg, and Pb with values ranged between 0.11-0.20mg/kg (liver), 0.09-0.17mg/kg, and 0.04-0.08mg/kg (muscle). The values of the various metals were significantly different ($P<0.05$) among the fish tissues. The mean levels profile for the metals in *P. peroteti* was as follows: Liver: Zn > Ni > Cd > As > Mn > Pb ; Kidney: Zn > Mn > Ni > Cd > As > Pb; Muscle: Zn > Ni > Cd > As > Mn > Pb.

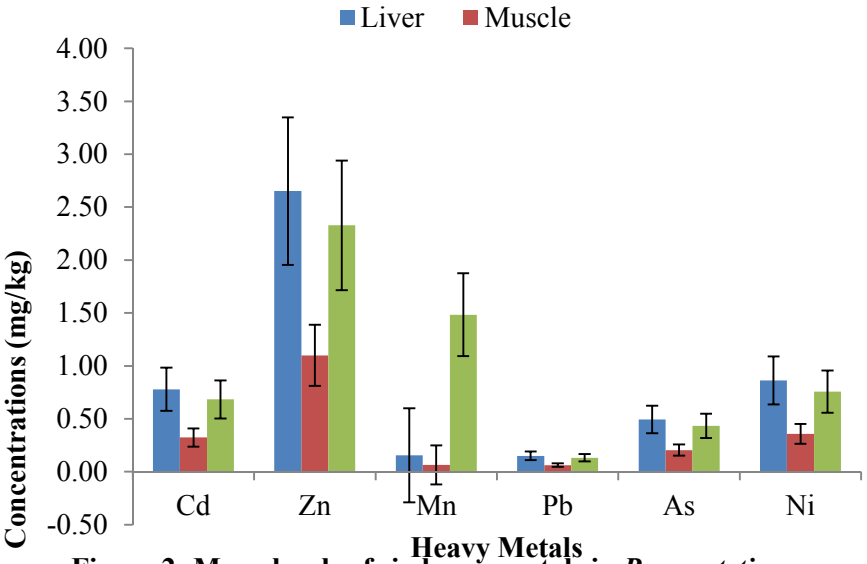

Figure 2: Mean levels of six heavy metals in *P. peroteti*

The oral reference doses for the heavy metals and the target hazard quotients (THQs) of studied metals through the consumption of *A. vulpes* and *P peroteti* for residents are shown in table 2. Target hazard quotients (THQs) for Cd, Pb, As, Ni, Mn and Zn were 0.0411, 0.0021, 0.0476, 0.0023, 0.0002 and 0.0005 for P. peroteti; 0.0010, 0.0007, 0.0214, 0.0006, 0.0001 and 0.0001 for A. vulpes. The total THQ (TTHQ) of *P. peroteti* and *A. vulpes* were 0.0938 and 0.0239 respectively. TTHQ in both fish species less than 1, suggesting that the consumption of *P. peroteti* and *A. vulpes* are unlikely to cause any adverse health effects to consumers.

Table 2: THQs of the studied heavy metals in *A vulpes* and *P. peroteti*

Element	RfDo	THQ *A vulpes*	THQ *P. peroteti*
Cd	0.001	0.0010	0.0411
Pb	0.0036	0.0007	0.0021
As	0.0003	0.0214	0.0476
Ni	0.02	0.0006	0.0023
Mn	0.14	0.0001	0.0002
Zn	0.3	0.0001	0.0005
	TTHQ	0.0239	0.0938

Discussion

In this study, the *A. vulpes* and *P. peroteti* showed the presence of heavy metal concentrations in their liver, muscle and kidney. In both fishes studied, the highest concentration of Cd, Zn, Pb, Mn, As, and Ni occurred in the liver while the lowest concentrations of these metals occurred in the muscle. The high levels of heavy metals in the liver as shown in this study could be due to the physiological role played by this organ in the detoxification of xenobiotics. Findings from this study indicate that the mean concentrations of Cd in the liver, muscle and kidney were 0.2, 0.08, and 0.18mg/kg in *A. vulpes* and 0.78, 0.32 and 0.68mg/kg in *P. peroteti* respectively. Conversely, low levels of Cd was recorded in fishes of Ikpoba River, Benin City, Nigeria [12]. Cadmium has been known to cause serious health effects in fish. In man, cadmium poisoning could lead to anemia, renal damage, bone disorder and cancer of the lungs [13]. Mean concentrations of Zinc in the liver, muscle and kidney were 0.69, 0.29, and 0.61mg/kg in *A. vulpes* and 2.65, 1.10 and 2.33mg/kg in *P. peroteti* respectively. Zinc toxicity is rare, but at concentrations in water up to 40mg/kg, may induce toxicity, characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite, and nausea. The mean concentrations of Pb in the liver, muscle and kidney were 0.04, 0.02, and 0.03mg/kg in *A. vulpes* and 0.15, 0.06 and 0.13mg/kg in *P. peroteti* respectively. Daka *et al*. [14] recorded low levels of Pb in fish species from Azuabie Creek in the Bonny Estuary, Nigeria. Pb is a toxic element which have no significant biological functions and show their carcinogenic effects on aquatic biota and humans even at low exposures. In this study, Mn mean concentrations in the liver, muscle and kidney were found to be 0.16, 0.06, and 0.14mg/kg in *A. vulpes* and 0.59, 0.25 and 0.52mg/kg in *P. peroteti* respectively. Mn in larger amounts, can cause neurological damage which is sometimes irreversible [15]. From the results of this study, mean concentrations of Arsenic in the liver, muscle and kidney were found to be 0.13, 0.05, and 0.11mg/kg in *A. vulpes* and 0.49, 0.2 and 0.43mg/kg in *P. peroteti* respectively. Arsenic has been reported to cause severe damage to the renal and nervous systems of fish as well as gill damage (severe destructive pathological changes, i.e. structural lesions) [16]. In humans, Arsenic has been reported to be associated with hypertension and serious impacts on the cardiovascular system, and even hepatic damage at high doses [17,18). In this study, mean concentrations of Ni in the liver, muscle and kidney were found to be 0.23, 0.09, and 0.20mg/kg in *A. vulpes* and 0.86, 0.36 and 0.76mg/kg in *P. peroteti* respectively. Idodo-Umeh [19] reported low levels of Ni in some fishes from Olomoro water bodies. Also, Oronsaye *et al.* [20] also recorded low levels in *Mormyops deliciosus* and *Mormyrus mactrophthalmus* from Ikpoba river dam. Ubalua *et al* [21] reported low levels of heavy metals in some fish and shellfish of Aba River Abia State, Nigeria. The levels were below US EPA standards except for lead, iron and mercury.

P. peroteti had higher concentrations of heavy metals compared with *A. vulpes*. Babatunde *et al.,* [22] reported differential bioaccumulation of heavy metals by fish of different species. Murtala *et al.* [23] studied the accumulation of some heavy metals in the operculum, gills, heart, kidney, muscle and vertebrae of some fishes collected from fishermen around Ogun Estuary; and reported that *Clarias gariepinus* accumulated less heavy metal than *Hydrocynus forskahlii* and *Hyperopisus bebe occidentalis*. Accumulation of heavy metals vary considerately among metals and species [24]. The THQ values for *P. peroteti* was in the order As>Cd>Ni>Pb Zn>Mn while for *A. vulpes* was in the order As>Cd>Pb>Ni>Zn=Mn. The highest THQ values were for Arsenic with the values 0.0476 and 0.0214 for *P. peroteti* and *A. vulpes* respectively. The least THQ values were for Mn with values 0.0002 and 0.0001 for *P. peroteti* and *A. vulpes* respectively. Arsenic was the major risk contributor while Mn was the least for both fish species studied. The total THQ (TTHQ) of *P. peroteti* and *A. vulpes* were 0.0938 and 0.0239 respectively. TTHQ in both fish species less than 1, suggesting that the consumption of *P. peroteti* and *A. vulpes* are unlikely to cause any adverse health effects to consumers.

Conclusion: In this study, the anadromous fishes *A. vulpes* and *P. peroteti* showed the presence of heavy metal concentrations in their liver, muscle and kidney. The total THQ (TTHQ) of *P. peroteti* and *A. vulpes* were 0.0938 and 0.0239 respectively. TTHQ in both fish species less than 1, suggesting that the consumption of *P. peroteti* and *A. vulpes* are unlikely to cause any adverse health effects to consumers.

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