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Spectrometric Analysis of Heavy Metals in Some Fish Species and Sediments from River Ibi, Taraba State

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Abstract
The study uses experimental methods in carrying out the research. The research aimed at examining "Spectrometric Analysis of Heavy Metals in Some Fish Species and Sediments from River Ibi, Taraba State" Despite the increasing interest and continuing experimental success around Taraba State (Nigeria), determination of heavy metal concentration in fish and its sediment has not been fully achieved. Therefore, the determination of heavy metal in the aquatic environment has becomes a public health undertaking worldwide during recent years. However, several rivers in Nigeria have not been adequately assessed for heavy metals concentration. Hence, this study assesses the concentration of heavy metals in fish species (Heterotis niloticus, Lates niloticus, Pampus argenteus, Clarias gariepinus and Oreochromis niloticus) and it's sediment from River Ibi (in Taraba State) using Microwave plasma Atomic Emission Spectroscopy (MP- AES). Result for Iron showed that some are within the permissible limit approved by WHO while others are more than the approved limit by FAO/WHO. High concentration of heavy metals (Zinc, Lead, Cadmium, Chromium and Iron.) in fish could lead to kidney, liver, cancer, tooth, amongst others related health issues in humans if consumed. The study recommended among others, that fishes should be examined properly before introduction into the market for sales and consumption and that enlightenment programs should be created for fishermen and fish sellers in Taraba State on proper handling of fish meant for human consumption so as to avoid exposure to toxic metals.
Keywords: Spectrometric-Analysis, Heavy-Metals, Fish, Species and Sediments.

Introduction

Heavy metals are a group of metals and metalloids that have relatively high density and are toxic even at parts per billion levels (ppb) [1]. Examples include Pb, As, Hg, Cr, Cd, Zn etc. Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Sediment is solid material that is moved and deposited in a new location. Sediment can consist of rocks and minerals, as well as the remains of plants and animals. It can be as small as a grain of sand or as large as a boulder. Sediment moves from one place to another through the process of erosion [2]. This study aimed to provide information on the microwave spectroscopic analysis of heavy metals in some fish species and sediments from river Ibi, Taraba State, Nigeria.

Microwaves (μ-waves) are types of electromagnetic radiation with frequencies ranging from approximately 300 MHz (0.3 GHz) to 300 GHz. They lie between radio waves and infrared light on the electromagnetic spectrum. Spectroscopy of heavy metals involves studying the interaction of electromagnetic radiation with the metal atoms or ions. This technique is used to analyze the electronic structure and energy levels of the metal atoms by observing the absorption, emission, or scattering of light. Heavy metals have complex electron configurations, leading to rich spectral lines in the UV-visible and X-ray regions [3]. The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms [4]. The contamination of water bodies with a variety of pollutants has become an issue of concern over the last few decades, not only because of the threat to public water supplies, but also the hazards to human consumption of fishery resources and other aquatic biotas [5]. Heavy metals are natural trace components of the aquatic environment and enter the aquatic environment through the earth crust, which has led to a steady-state background level in the aquatic environment. As a result of anthropogenic activities, the concentrations of heavy metals have increased [6], and their accumulation leads to heavy metal contaminations in the aquatic system. Being non- biodegradable, the heavy metals can be concentrated along the food chain, producing their toxic effect at points far away from the source of pollution [7].

River could be contaminated by heavy metal as a result of industrial and agricultural waste and by-product. High concentrations of heavy metals are toxic to the water, soil, and air. Fishes in the river are an important food source for the population, heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have the potential to be toxic to living organisms [8].

Fish are aquatic vertebrate animals that have gills but lack limbs with digits, like fingers or toes. Fish play key roles in ecosystems because they are vertebrates, which are at the top of the food chain [9]. Among other contaminants, heavy metals such as arsenic, cadmium, chromium, Lead, and copper are highly toxic to human cells [10]. Fish sample can be considered as one of the most significant indicators in fresh water systems for the estimation of metals pollution level [11]. The essential metals must be taken up from water, food or sediment. These essential metals can also produce toxic effects when the metal intake is excessively elevated [12].

Site description

The River Ibi (in Taraba State) is the location for this study. Taraba is a state in North Eastern Nigeria, named after the Taraba River with coordinates: 8°00'N 10°30'E, population (2006 Census) is 2,294,800. The Benue, Donga, Taraba and Ibi rivers are the main rivers in the state. These rivers rose from the Cameroonian mountains, spanning almost the entire length of the state in the North and South direction to link up with the River Niger. River Ibi is located in southern part of Taraba.

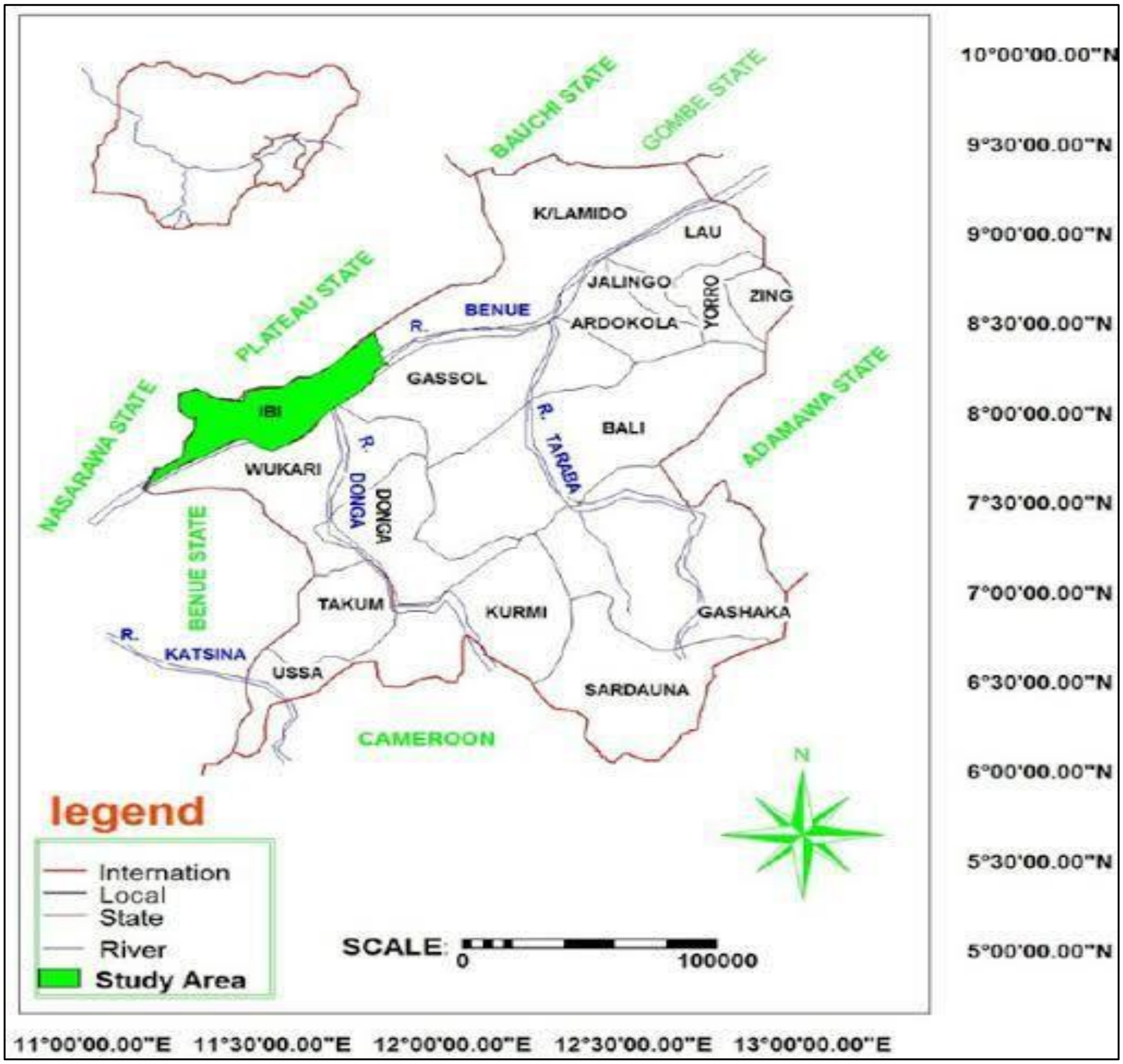

Figure 2: Map of Taraba State Showing River Ibi, Ibi LGA

Collection of fish and sediment samples

Collection of fish and sediment samples were carried out during wet and dry season within River Ibi. Fish samples were collected using Gill nets with the help of the fisher men, the sediment were collected in two different location (river bank and middle of the river) using iron pipe to the depth of 2 m for both wet and dry season, water was also collected in wet and dry season. All samples were labelled and placed in an ice- cold box accordingly before transported to the laboratory. Each fish sample was weighed, cut and separated from their bones and then washed with deionize water.

Fish and sediment samples preparation and preservation

After washing fish samples with deionized water, fish and sediment samples were dried at room temperature for 1 week. The preserved fish samples and sediment samples were used because it is the major target for heavy metal analysis. The dried samples of the fish muscles, fish bones were grounded without skins using laboratory blender. The samples were sieved and put in a plastic container and stored until digestion.

MP-AES Optimization

After sample preparation, wavelength optimization was performed in order to select optional spectral wavelength for measurement. Multi element standard solutions from MP-AES Agilent 4200 analytical software was used.

Experimental Analyses

Analysis was carried out in Multi-User Laboratory in the Ahmadu Bello University Zaria. Instrumentation For this study is a microwave plasma atomic emission spectrometer, the Agilent 4200 MP-AES (Instrument MY15150001) was used for elemental determination of digested Fish and sediment samples.

Microwave Sample Digestion

Forty-six (46) different samples were extracted from fish species, soil and water in River Ibi, Taraba State and digested before analysis by MP-AES. To prepare the fish and sediment samples for microwave digestion, 0.5g of each powdered samples were accurately weighed and transferred to a 250mL conical flask, 5mL of nitric acid and 2mL of hydrochloric acid was added and digested. Microwave digestion of the samples was carried out in accordance with the following procedure: The digestion chamber was initially pressurized with industrial grade nitrogen gas, before the temperature and pressure were gradually increased to 240°C and 150bar respectively over 20 minutes. These values were maintained for a further 10 minutes (the duration of the digestion) to ensure complete digestion. Upon completion of the program each digested sample was diluted to a volume of 20ml with distil water.

Elemental Analysis

The Agilent 4200 MP-AES has superior performance compared to FAAS in terms of detection limits, linear range, and sample throughput. The 4200 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. The use of nitrogen improves safety by eliminating expensive, hazardous gases.

The instrument features mass flow control of the nebulizer gas, and a torch loader mechanism which automatically connects all gases. Method parameters was automatically optimized in the MP Expert software, which also features automatic background correction.

Plate 1: The Set-up of Agilent 4200 MP-AES

Results

Table 1: Concentration of Zn, Cr, Cd, Pb and Fe for Muscles in Big and Small Fish during Wet Season

S/N	SAMPLE	Zn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)
1	**BAFMWS**	22.3372	0.3141	0.0080	NF	16.5564
2	**SAFMWS**	18.5245	0.2306	0.0095	0.0193	10.3947
3	**BNFMWS**	46.7136	0.1915	0.0049	0.1066	8.6957
4	**SNFMWS**	21.6905	0.0804	0.0036	0.0091	4.5936
5	**BPFMWS**	37.4947	0.0932	0.0043	0.0778	9.5533
6	**SPFMWS**	37.7902	0.3006	NF	0.4545	11.6235
7	**BCFMWS**	40.9261	1.8239	NF	5.8825	18.2454
8	**SCFMWS**	47.4239	2.5844	NF	10.8206	22.5953
9	**BTFMWS**	29.7480	1.4195	NF	3.8717	25.3708
10	**STFMWS**	18.2746	1.7443	NF	13.5276	21.0372

MWS = Muscles Wet seasons
BAF = Big Arowana fish, SAF= Small Arowana Fish BNF= Big Nile perch fish, SNF = Small Nille perch fish BPF = Big pomfret fish, SPF = Small pomfret fish
BCF = Big Cat fish, SCF = Small Cat fish
BTF = Big Tilapia fish, SBT = Small Tilapia fish NF= Not Found

Table 2: Concentration of Zn, Cr, Cd, Pb and Fe for muscles in Big and Small Fish during Dry Season

S/N	SAMPLE	Zn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)
1	**BAFMDS**	35.8754	0.1230	NF	0.0812	7.8037
2	**SAFMDS**	26.5442	0.1817	0.0093	0.1946	9.5558
3	**BNFMDS**	48.2168	0.2054	0.0067	0.0629	7.5757
4	**SNFMDS**	55.5239	0.2572	0.0015	0.0633	12.4873
5	**BPFMDS**	47.6379	0.1489	0.0031	0.0574	11.7522
6	**SPFMDS**	38.2709	1.7027	NF	0.2106	182.0322
7	**BCFMDS**	44.1245	2.0139	NF	5.2991	187.3833
8	**SCFMDS**	62.5467	2.5311	NF	9.6329	220.4226
9	**BTFMDS**	18.1619	1.6671	NF	1.9892	270.1638
10	**STFMDS**	15.0783	1.8517	NF	1.9503	68.1695

MDS = Muscles Dry seasons
BAF = Big Arowana fish, SAF= Small Arowana Fish BNF= Big Nile perch fish, SNF = Small Nille perch fish BPF = Big pomfret fish, SPF = Small pomfret fish
BCF = Big Cat fish, SCF = Small Cat fish
BTF = Big Tilapia fish, SBT = Small Tilapia fish NF= Not Found

Table 3: Concentration of Zn, Cr, Cd, Pb and Fe for Bones in Big and Small Fish during Wet Season

S/N	SAMPLE	Zn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)
1	**BAFBWS**	42.1260	0.9541	0.0122	NF	5.1907
2	**SAFBWS**	17.9344	0.1085	0.0085	NF	10.7386
3	**BNFBWS**	27.7068	0.2019	0.0072	NF	10.5038
4	**SNFBWS**	31.8386	0.1622	0.0049	NF	9.1450
5	**BPFBWS**	28.7767	0.0585	0.0009	0.0056	7.3671
6	**SPFBWS**	35.1331	0.0954	0.0042	NF	9.2540
7	**BCFBWS**	42.0195	2.4142	NF	1.7194	230.2863
8	**SCFBWS**	41.8657	2.2102	NF	1.3503	239.5169
9	**BTFBWS**	20.2715	5.0052	0.2187	0.5668	420.2117
10	**STFBWS**	9.4574	NF	NF	2.3056	34.5228

BWS = Bones Wet Seasons
BAF = Big Arowana fish, SAF= Small Arowana Fish BNF= Big Nile perch fish, SNF = Small Nille perch fish BPF = Big pomfret fish, SPF = Small pomfret fish
BCF = Big Cat fish, SCF = Small Cat fish
BTF = Big Tilapia fish, SBT = Small Tilapia fish NF= Not Found

Table 4: Concentration of Zn, Cr, Cd, Pb and Fe for Bones in Big and Small Fish during Dry Season

S/N	SAMPLE	Zn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)
1	**BAFBDS**	30.6289	0.2214	0.0067	0.0750	10.4034
2	**SAFBDS**	22.0406	0.2385	0.0089	NF	6.8575
3	**BNFBDS**	35.5034	0.1461	0.0035	NF	9.7067
4	**SNFBDS**	20.7985	0.0857	0.0066	NF	3.3453
5	**BPFBDS**	36.2390	0.1221	0.0045	0.0695	22.8221
6	**SPFBDS**	32.7872	0.0664	0.0011	NF	6.0809
7	**BCFBDS**	50.1634	2.8958	NF	12.3875	269.7309
8	**SCFBDS**	22.5464	NF	NF	4.7025	48.7574
9	**BTFBDS**	17.9146	2.5856	NF	4.9806	219.8183
10	**STFBDS**	19.8166	NF	NF	0.1482	188.9191

BDS = Bones Dry Seasons
BAF = Big Arowana fh, SAF= Small Arowana Fish BNF= Big Nile perch fish, SNF = Small Nille perch fish BPF = Big pomfret fish, SPF = Small pomfret fish
BCF = Big Cat fish, SCF = Small Cat fish
BTF = Big Tilapia fish, SBT = Small Tilapia fish NF= Not Found

Table 5: Concentration of Zn, Cr, Cd, Pb and Fe For Soil during Wet and Dry Season

S/N	SAMPLE	Zn (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)
1	SWS	0.0367	0.6305	NF	2.8416	920.8329
2	SBWS	0.1602	4.8059	NF	3.4393	5489.8102
3	SDS	0.2992	2.5581	NF	2.6649	3231.3855
4	SBDS	0.0066	4.8124	NF	5.8760	5343.7916

WS/DS = Wet / Dry Season

SWS= Soil Wet Season, SBWS = Soil Bank Wet Season

SDS = Soil Dry Season, SBDS = Soil Bank Dry Season

Table 6: Concentration of Zn, Cr, Cd, Pb and Fe for Water during Wet and Dry Season

S/N	SAMPLE	Zn (mg/L)	Cr (mg/L)	Cd (mg/L)	Pb (mg/L)	Fe (mg/L)
1	WDS	0.1645	NF	0.0151	NF	NF
2	WWS	0.2261	0.0096	0.0147	NF	NF

WS/DS = Wet / Dry Season

WDS= Water Wet Season, WWS= Water Wet Season

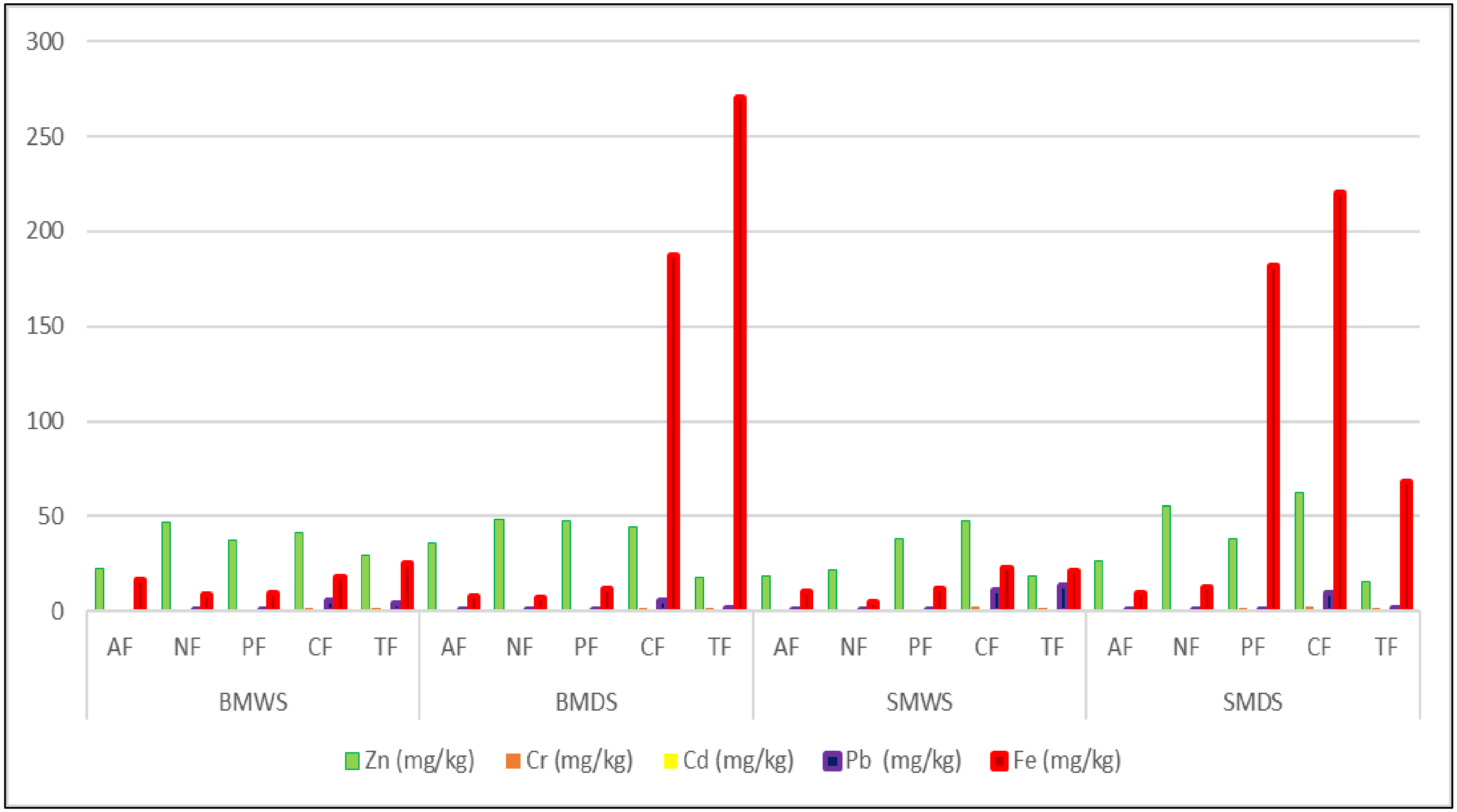

Figure 3: Show Concentration of Zn, Cr, Cd, Pb and Fe Muscles of Big and Small Fish for Wet and Dry Season

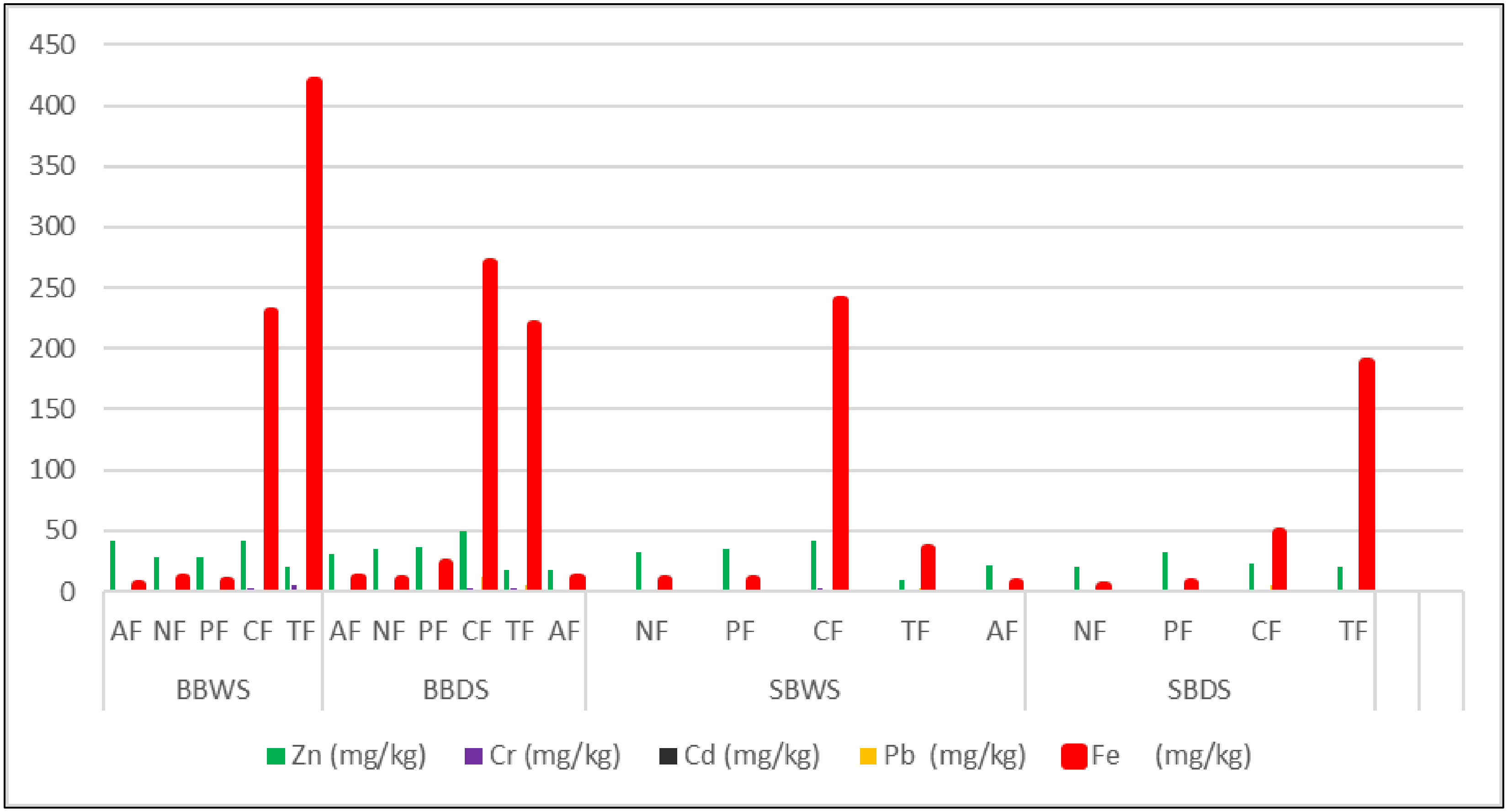

Figure 4: Concentration of Zn, Cr, Cd, Pb and Fe of Bones of Big and Small Fish for Wet and Dry Season

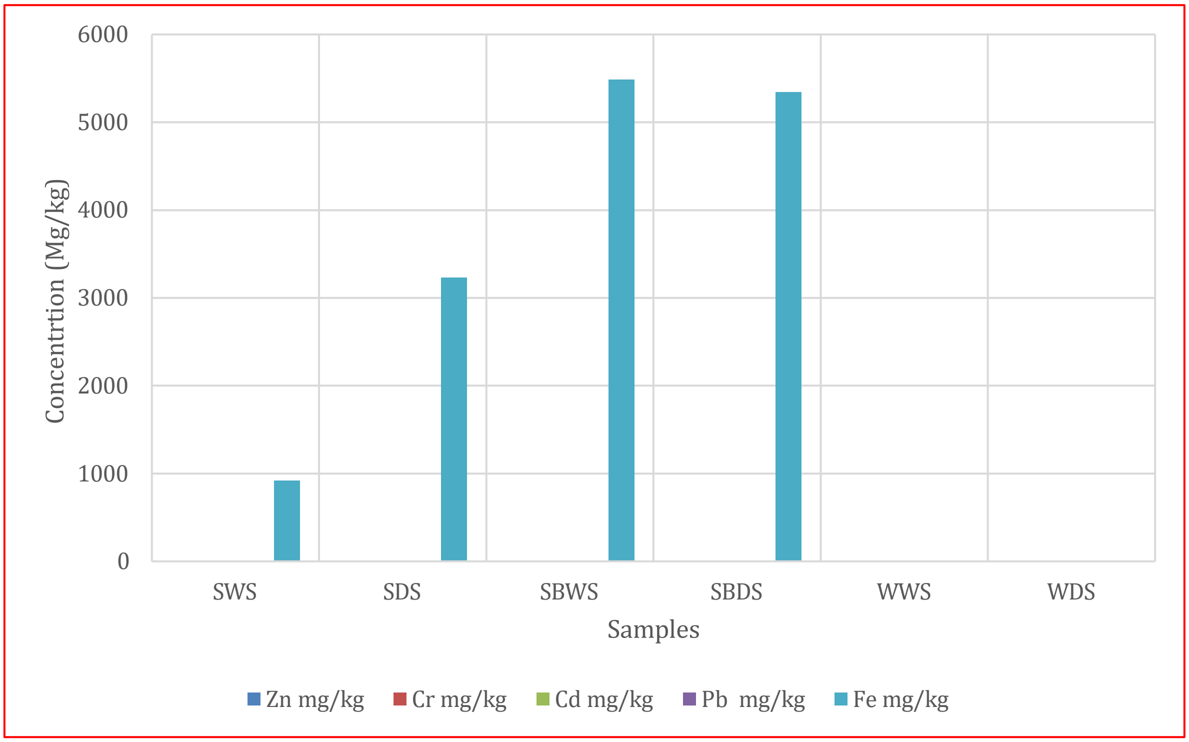

Figure 5: Concentration of Zn, Cr, Cd, Pb and Fe for Sediment and Water Samples in both wet and Dry Seasons Key

WS/DS = Wet / Dry Season
SWS= Soil Wet Season, SBWS = Soil Bank Wet Season SDS = Soil Dry Season, SBDS = Soil Bank Dry Season WDS= Water Wet Season, WWS= Water Wet Season

Discussion

The Zn contents compared for the big and small muscles and bones in wet and dry season for all fish samples tested ranged between 9.45 – 62.54 mg/kg. All the values of fish samples examined had zinc content within the 100 mg/kg permissible limit set by [13]. Similar low concentration of Zinc was reported by [14], the highest concentration of Zn (12.02±0.02 mg/kg), was obtained in catfish gills harvested at the major storm drain station

Chromium uptake in fish primarily occurs through gill absorption and ingestion of contaminated particles or prey items [15]. Once absorbed, chromium can accumulate in fish tissues, with higher concentrations typically observed in organs such as the liver, gills, kidneys, and muscles [16]. Chromium exposure to humans primarily occurs through ingestion of contaminated food and water, inhalation of airborne particles, and dermal contact with chromium- containing products [17]. Excessive intake of chromium (Cr) can lead to adverse health effects, including respiratory irritation, allergic dermatitis, and gastrointestinal disorders [18]. Long-term exposure to high levels of Cr has been associated with increased cancer risk, particularly lung cancer.

Chromium content for big and small muscle and bone in all fish samples collected ranges from 0.05 – 5.0mg/kg. The lowest and highest values of this element were observed in big (*Pampus argenteus) in wet season* and big (*Oreochromis niloticus*) in wet season respectively. The fish samples examine had Cr content higher than the 0.05 – 0.15mg/kg permissible limit set by [19] except for species of big *Pampus argenteus* which was within the acceptable limit. This therefore implies that the consumption of fish species examined in this study other than (*Pampus argenteus*) would pose health risk associated to Chromium in human system, reasons could be stationary fuel combustion (residential, commercial), leaching from topsoil and rocks entry into bodies of water and also the release to soil metal processing facilities. A similar higher concentration of chromium was reported by [20] in Abare River of Zamfara state to be 1.313 mg/kg. Likewise, [21] reported 0.77 mg/kg in gills of catfish sample from Njuwa lake of Adamawa State.

Cadmium content of fish samples collected ranges from 0.001 - 0.21mg/kg. The lowest and highest values of this element were observed in big bone (*Pampus argenteus*) in wet season and big bone *(Oreochromis niloticus*) in wet season respectively were above the [19] permissible limit of 0.05mg/kg for Cd contents in (*Oreochromis niloticus*) except for (*Pampus argenteus*) which was within permissible limit. Cd was however not detectable in the soil samples examined. In a study by [20], a higher value of Cadmium (0.904 mg/kg) was reported in catfish liver from Bakolori dam of Zamfara State. Similarly, a higher value for Cadmium was obtained by [22] in a tilapia sample from a river in Libya to be 7.41 ± 1.45 mg/kg. The high level of Cd above the findings of the present work, as reported above could be due to accumulation of the metal in water bodies as a result of agricultural or anthropogenic activities taking place around the water source. The concentrations of Cd in fish analyzed in this research were within the 0.01 mg/kg maximum permissible level in fish [19].

Lead (Pb) content of fish samples collected ranges from 0.005 - 13.52mg/kg. The lowest and highest values of this element were observed in small bone (*Pampus argenteus)* and small muscle (*Oreochromis niloticus)* both are in wet season. The fish samples examined had Pb content higher than the 0.5 – 0.6mg/kg permissible limit set by [19] except for species of small bone (*Pampus argenteus)* which was within the acceptable limit, here high value could be due to human activities, and vehicle movement that occur in the environment or migrated from a different river. Findings from the study revealed that Pb contents were not detected in the water samples collected from River Ibi however, Pb concentration in soil from River Ibi ranges from 2.66mg/kg – 5.87mg/kg. This concentration is below [19] permissible limit of 85mg/kg for Pb concentration in soils.

The study found out that Fe concentration collected ranged from 3.3400 – 5489.8102 mg/kg in fish bone (*Lates niloticus*) in dry season and soil (sediment bank) in wet season samples from river Ibi were within the permissible limits set by [19] for both Fe concentration in fish and soil. This therefore implies that fish species from river Ibi contains recommended Fe contents, hence, consumption of the studied fish species can serve as a cofactor for enzymes involved in oxygen transport, energy metabolism, and antioxidant defense mechanisms.

The following fish samples, SPFMDS (182.03 mg/kg), BCFMDS (187.38 mg/kg), STFBDS (188.91 mg/kg), BTFBDS (219.81 mg/kg), SCFMDS (220.42 mg/kg), BCFBDS (269.73 mg/kg), (270.16 mg/kg), BCFBWS (230.28 mg/kg), SCFBWS (239.51 mg/kg), BTFBWS (420.21 mg/kg) had high Fe values that is above maximum Permissible limit of Fe in fish 100 mg/kg [19]. Therefore, these fishes are not advisable for consumption and it may be as a result of weight of the fishes, feeding mood, sewage from the traders/passengers, agricultural urban runoff and some may have migrated from a different area.

Conclusion

The study investigates the concentration of heavy metal in some fish, soil and water samples during wet and dry season from River Ibi, Taraba state. Results obtained from this study showed the presence of Zn, Cr, Cd, Pb, and Fe in the samples collected and examined. Highest concentration of Zinc contents was observed in small muscle *(Clarias gariepinus)* during dry season. The highest amount of Lead was found in small muscle *(Oreochromis niloticus)* during wet season while Chromium, Cadmium and Iron contents were observed in big bone *(Oreochromis niloticus)* and soil bank during wet season respectively. This was above the permissible limit set by [19]. Highest Zinc (dry season) and lead (wet season) concentration were found in both small muscle of *Clarias gariepinus and Oreochromis niloticus* respectively. Based on the findings from this study, *Heterotis niloticus, Lates niloticus and Pampus argenteus* were most safe for consumption while consumption of *Clarias gariepinus and Oreochromis niloticus* could lead to toxic effect to consumers.

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