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Metal Pollutants Distribution and Bioaccumulation in Two Ecological Important Fisheries Resources; *Chrysichthys nigrodigitatus* and Callinectes *latimanus* From Porto-Novo Lagoon Ecosystem, Benin Republic

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Abstract – **Quantitative distribution of metal pollutants and bio-accumulation in *Chrysichthys nigrodigitatus* and *Callinectes latimanus* from Porto-Novo Lagoon ecosystem was investigated during rainy and dry seasons. Metal pollutants including Hg, Cd, Cu, Zn, Cr, Fe, Mn, Pd, Ni, Va, and Methyl mercury were found in measurable quantities in the tissues/organs of test animals using AAS equipment and was above permissible limits of WHO, USFAD, EU and NRS. The metal pollutants (mg/kg) found in *Chrysichthys nigrodigitatus* were as follows: Hg = (0.0024±0.002, 0.0014 ±0.001), Cd = (1.106±0.16, 0.042±0.09), Cu = (3.69±7.6, 0.986±1.14), Zn = (46.64±15.1, 2.736±4.25), Cr=(46.64±15.1, 2.736±4.25), Fe = (81.43±44.6, 50.143±64.9), Mn=(10.67±7.6, 3.877±3.17), Pd = (39.71±22.2, 0.123±0.14), Ni=(9.50±2.5, 17.789±29.7), Va=(0.02±0.004, 0.004±0.001), Methyl mercury=(0.0015±0.001, 0.0003±0.0001). While the one found in *Callinectes latimanus* were as follows : Hg = (0.001±0.001, 0.001±0.0005), Cd=(7.87±7.31, 0.47±1.04), Cu = (8.12±5.98, 2.56±1.93), Zn=(45.82±23.02, 5.06±4.46), Cr = (45.82±23.02, 5.06±4.46), Fe=(69.51±63.19, 236.61±294.68), Mn=(20.87±10.61, 55.32±91.02), Pd=(47.52±50.67, 79.66±126.42), Ni=(12.09±3.28, 0.86±1.65), Va=(0.004±0.002, 0.001±0.0009), Methyl mercury = (0.001±0.0005, 0.0002±0.0002). There is a significant difference in the metals pollutants in the tissue and organs of *Chrysichthys nigrodigitatus* and *Callinectes latimanus* from Porto-Novo Lagoon ecosystem during rainy and dry seasons at 5% level of significance. The findings showed that *Chrysichthys nigrodigitatus* and *Callinectes latimanus* from Porto-Novo Lagoon bio-accumulate metal pollutants, which might affect human health as well as the physiology of the fin and shell fishes in the ecosystem. Regulatory bodies on environmental pollution are hereby enjoined to wake up to their statutory duties on environmental protection in order to stem the tide of these metal pollutants in the Porto-Novo Lagoon ecosystem.**

Keywords – **Bio-accumulation, *Chrysichthys nigrodigitatus*, *Callinectes latimanus*, Metal Pollutants, Porto-Novo lagoon.**

I. Introduction

The world industrial and technological advancement in the face of world population explosion has opened the floodgate of pollution into our environment, and our water bodies have been one of the major recipients of these pollutants. Coastal pollution has been increasing significantly over the recent years and found expanding environmental problems in many developing countries. Urban and industrial activities in coastal areas introduce significant amount of trace metals into the marine environment, causing permanent disturbances in marine ecosystems leading to environmental and ecological degradation and constitute a potential risk to a number of flora and fauna species, including humans, through food chains [1].

Heavy metals were chosen as suitable pollutants because they are widespread environmental contaminants, from either natural or anthropogenic sources, and are widely believed to be a threat to the health and survival of many marine or aquatic animals, including crustaceans [1]. The biological effect of trace metals in the lagoon ranges from beneficial stimulation to harmful retardation and death. Some trace metals including Cu, Mn, Fe and Zn are essential for good health and normal growth playing important roles in key metabolic activities in plants and animals such essential elements only become toxic when their concentration exceed the trace amounts required for normal metabolism [18].

The rate of bio-accumulation of heavy metals in aquatic organisms depends on the ability of the organisms to digest the metals and the concentration of such metal in the river. Also it has to do with the concentration of the heavy metal in the surrounding soil sediments as well as the feeding habits of the organism. Aquatic animals (including fish) bio-accumulates trace metals in considerable amounts and stay over a long period. Fishes have been recognized as good accumulators of organic and inorganic pollutants [15]. Moreover, since most organisms lack the ability to metabolize and excrete trace metals on absorption, these metals accumulate in the cells and tissues of exposed organisms and may be magnified along food chains [9].

Anthropogenic activities, such as mining, fossil fuel combustion or industrial processes, have greatly altered the biogeochemical cycles of trace metals and enhanced their bioavailability [11]. At elevated concentrations or availability, certain trace metals maybe toxic indeed, many metals are required by organisms but can have deleterious effects at high concentrations. Standards and guidelines for metal pollutants in the environment are aimed at protecting human health and aquatic life.

Porto Novo Lagoon, an arm of Gulf of Guinea is located at the capital of Republic of Benin. The estimate terrain elevation above sea level is 0 metre. Latitude: 6°28'0.01" Longitude: 2°36'0" [21]. In Benin, the complex Porto-Novo Lagoon is one of the largest lakes in West Africa with high productivities and exploitation [21]. With the sea, and run parallel to the coast behind the dune. There are about 72 species of both fin and shell fishes in the Porto Novo Lagoon [16] - [17].

The catfish, *Chrysichthys nigrodigitatus* (Lacépède), asiluroid fish of the family Bagridae is widely distributed in fresh and brackish waters in West Africa [19] - [14]. *Chrysichthys nigrodigitatus* is important both in ecological and economical terms, playing salient role in determining the dynamics and structure of aquatic ecosystem and is valued as food for man; serving as delicacy for many low income earners as it is cherished for its taste and affordable price [4]. *Callinectes latimanus* belong to family Potunidae. They are bottom dwelling aquatic crabs which are common constituents of tropical and subtropical estuarine system. *Callinectes latimanus* known as swimming crabs are one of the edible crabs in Benin Republic. Because of the role *Chrysichthys nigrodigitatus* and *Callinectes latimanus* plays in trophic chain, this makes them important in pollution study especially in bioaccumulation of metal pollutants in their tissues.

II. Materials and Methods

A. Description of Study Site

The Lagoon of Porto-Novo is a basin of up to 6meters, located in the South-East of the Republic of Benin (6º 27'N, 2º 36'E), Porto-Novo lagoon has a surface area of 17.52 km^2 and maximum length of 6km and maximum width of 4km (Figure 1). Porto-Novo lagoon is linked to Nokoue lagoon in the east through tatche where Porto-Novo lagoon receives the major inflow which characterizes the main hydrological regime of Porto-Novo lagoon seasonal tidal and salinity range.

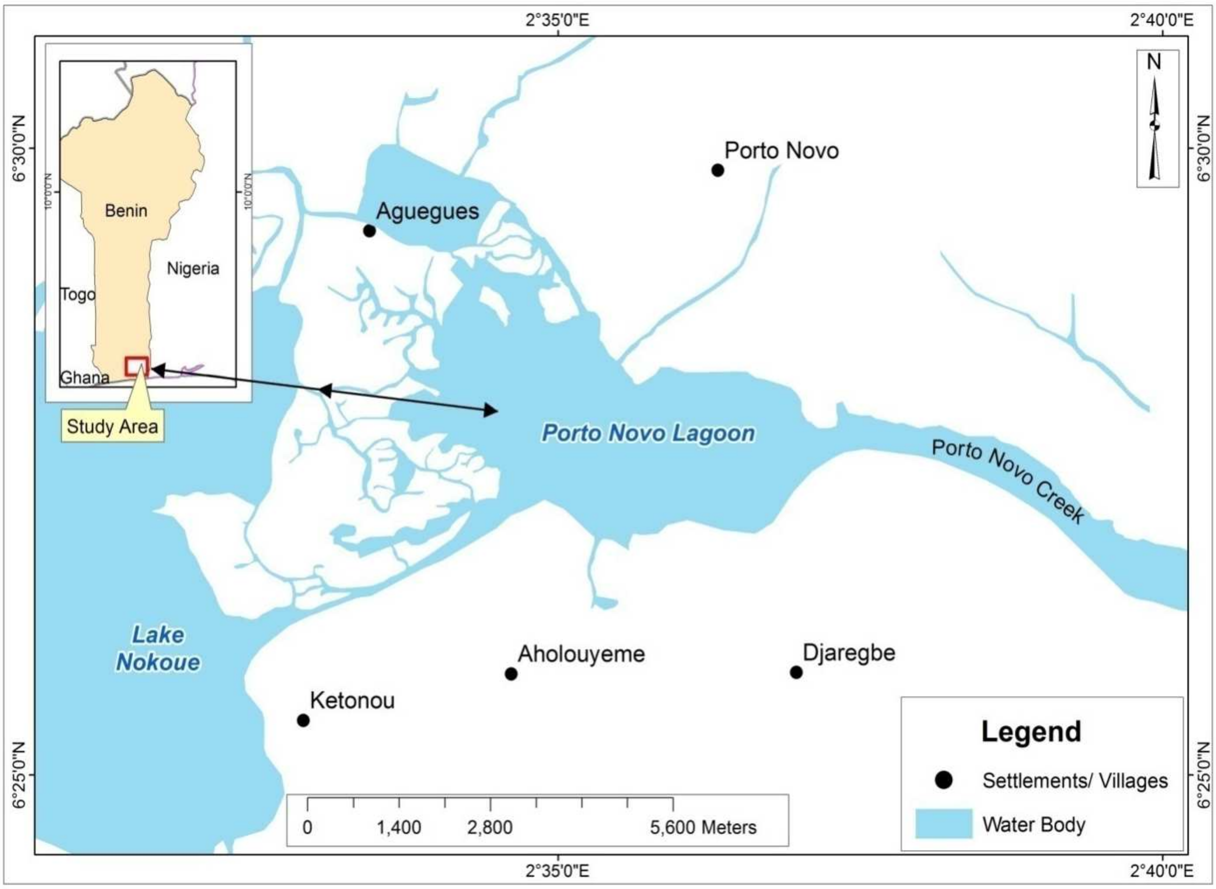

Fig. 1. Goe-Referenced Map of Porto-Novo Lagoon

B. Sampling Duration

Data were collected for 12 months, between July 2014 and June 2015 representing a complete hydrological cycle. These data were analyzed based on rainy and dry seasons respectfully.

C. Collection of Fin Fish and Shell Fish Samples

A stratified random sampling method was adopted in collection of mixed sexes of *Chrysichthys nigrodigitatus* and *Callinectes latimanus* of uniform sizes of 45.5g and 7.5 g respectively from " Djassin" main fish landing site cum market. Fin and Shell fish samples were kept in polythene bags respectively and stored in an iced cooler (<4^{o}c) for the analyses of selected metal pollutants as cited by [2]. Metal pollutants that were investigated during the period in view are Hg, Cd, Cu, Zn, Cr, Fe, Mn, Pd, Ni, Va, and methy mercury. All chain of custody was duly observed as cited by [8].

D. Analytical Methods

The methods of [13] were used to determine levels of (Hg, Cd, Cu, Zn, Cr, Fe, Mn, Pd, Ni, Va, and methyl mercury) trace metals in fish tissues. Digestions of test animal for metal pollutants were carried out separately using Atomic Absorption Spectrophotometer (Model Thermo Electron Corporation, S series AA Spectrometer with Gravities furnace, UK) as described by [5]. Twelve samples each of Chrysichthys *nigrodigitatus* and

Callinectes latimanus of average weight of 45.5g and 7.5g respectively were collected from commercial landing site and transported in iced box cooler for digestion and AAS laboratory procedures. Tissues/organs of interest are weighed. 5g each of tissue/organ sample from all the samples were weighed and put in a conical flask of about 250ml capacity then added 25ml of digesting reagent (Nitric acid and Hydrogen peroxide) in ratio 1:1 and place on a hot plate under the fume cupboard and heat at a temperature not more than 120^{0}c .When the sample is about 5ml in the conical flask bring it down and allow to cool. Filter the sample using the wotman I filter paper into a 50ml standard volumetric flask then make up to mark and Set the sample for AAS (calibrated) for Trace Metals reading.

E. Statistical Analyses

To evaluate the significant difference in the bioaccumulation of metal pollutants in the test animals for a complete hydrological cycle, two-way ANOVA and Duncan multiple test were used.

III. Results and Discussion

The quantitative distribution of metal pollutants in *Chrysichthys* nigrodigitatus and *Callinectes latimanus* confirmed that all tested metal pollutants were present in quantifiable concentrations speckled in the organs/tissues of the test aquatic animals. The detected concentrations of metal pollutants in test aquatic animals are discussed according to international standard values of WHO and EEC [21], EU regulations and according to USEPA [20]. The roles *Chrysichthys nigrodigitatus* and *Callinectes latimanus* plays in trophic chain makes it important in pollution study especially in the study of bio-accumulation of metal pollutants in their tissues. The analysis of *Chrysichthys nigrodigitatus* and *Callinectes latimanus* for metal pollutants showed that all metal pollutants investigated were present in measurable concentrations that varied in-between the two seasons and within the organs and tissue (Gill, Liver/Hepatopancreas, bones/Carapace, Gut and Muscle) of *Chrysichthys nigrodigitatus* and *Callinectes latimanus* respectively (Tables 1 and 2).

Quantitative bio-accumulation of metal pollutants in the tissue of *Chrysichthys nigrodigitatus* are stated below in the order of magnitude; from highest to lowest. In rainy season, Fe =407.17, Cr =233.18, Zn =227, Pd =198.58, Mn =53.37, Ni =47.5, Cu =18.46, Cd =5.53, Va =0.112, Hg =0.012, MH_3Hg=0.0077. In dry season it follows this trend, Fe =250.717, Ni = 88.947, Zn =37.84, Mn =19.387, Cr =13.682, Cu =4.93, Cd =0.209, Pd =0.616, Va =0.019, Hg =0.007, MH_3Hg=0.0014. This shows that metal pollutants concentration in the organs of *Chrysichthys nigrodigitatus* from Porto-Novo lagoon is higher in the rainy season than dry season with the exception of Nickel and also varies within the organs (Table. 1)

Table 1. Total and Mean (± SD) of metal pollutants (mg kg-1 wet weight) in Chrysichthys *nigrodigitatus* from Porto Novo lagoon**.** PL Permissible limit (dry wt) according to FAO/WHO (1999) **µg/g

Hydrological Period	Tissue Type	Hg	Cd	Cu	Zn	Cr	Fe	Mn	Pd	Ni	Va	MH_3Hg
JULY-DEC 2014 **(Rainy season)**	GILL	0.001	1.33	0.4	47.27	54.76	78.38	10.90	26.80	10.80	0.028	0.001
	LIVER	0.002	1.23	17.30	44.70	61.36	140.16	2.23	42.97	8.24	0.025	0.0012
	BONE	0.001	1.04	0.15	90.41	48.7	39.28	22.12	35.47	10.00	0.023	0.0011
	GUT	0.006	0.96	0.11	38.65	21.62	110.83	12.30	17.70	5.89	0.017	0.0031
	MUSCLE	0.002	0.97	0.50	5.97	46.74	38.52	5.82	75.61	12.57	0.019	0.0013
	Total	**0.012**	**5.53**	**18.46**	**227**	**233.18**	**407.17**	**53.37**	**198.55**	**47.5**	**0.112**	**0.0077**
	Mean (± SD)	0.0024± 0.002^c	1.106± 0.16^c	3.69± 7.6^c	46.64± 15.1^b	46.64±1 5.1^b	81.43± 44.6^a	10.67± 7.6^c	39.71± 22.2^b	9.50± 2.5	0.02± 0.004^c	0.0015± 0.001^c
JAN-JUNE 2015 **(Dry season)**	GILL	0.001	0.001	1.21	7.88	0.26	13.68	5.925	0.086	0.185	0.005	0.0003
	LIVER	0.001	0.204	2.88	7.45	10.23	23.36	0.372	0.372	1.373	0.004	0.0002
	BONE	0.001	0.002	0.13	15.07	0.86	39.46	2.487	0.054	17.579	0.004	0.0002
	GUT	0.003	0.001	0.52	6.44	0.326	9.797	2.328	0.037	0.528	0.003	0.0005
	MUSCLE	0.001	0.001	0.19	1.00	2.006	164.42	8.275	0.067	69.282	0.003	0.0002
	Total	**0.007**	**0.209**	**4.93**	**37.84**	**13.682**	**250.717**	**19.387**	**0.616**	**88.947**	**0.019**	**0.0014**
	Mean (± SD)	0.0014 ± 0.001^b	0.042± 0.09^b	0.986± 1.14^b	2.736± 4.25^b	2.736±4. 25^b	50.143±6 4.9^a	3.877± 3.17^b	0.123± 0.14^b	17.789± 29.7^b	0.004± 0.001^b	0.0003± 0.0001^b
WHO /FAO (mg/day)		**0.5**	**0.1****	**3.0**	**60.0**	**50**	**43.0**	**2.0-9.0**	**0.214**	**2.45**	**0.5**	**0.0033**
USFDA Limit (mg kg-1)		**0.5**	**0.5**	**70**	**30**	**N/A**	**N/A**	**5.4**	**0.5**	**N/A**	**N/A**	**0.001**
EU regulation(mg kg-1)		**0.5**	**0.05**	**N/A**	**N/A**	**N/A**	**N/A**	**N/A**	**0.4**	**N/A**	**N/A**	**0.0016**
NRS (mg kg-1)		**0.5**	**N/A**	**0.5**	**N/A**	**N/A**	**N/A**	**N/A**	**0.5**	**N/A**	**N/A**	**0.0005**

N/A=Not Available

Concentration of metal pollutants bio-accumulation in the tissue of *Callinectes latimanus* are presented below in the order of magnitude; from highest to lowest. In rainy season, Fe =347.53, Pd =237.62, Cr =229.08, Zn =134.53, Mn =104., Ni =60.44, Cu =40.58, Cd =39.332, Va =0.01805, Hg =0.007, MH_3Hg=0.0033. In dry season it follows this trend, Fe =1183.05, Pd = 398.29, Mn =276.62, Cr =25.31, Zn =23.89, Cu =12.78, Ni=4.3, Cd =2.374, Va =0.0045, Hg =0.0043, MH_3Hg=0.001. This shows that metal pollutants concentration in the organs of *Callinectes latimanus* from Porto-Novo lagoon is higher in

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the rainy season than dry season with the exception of Cr and also varies within the organs (Table. 2).

Table 2. Total and Mean (± SD) of metal pollutants (mg kg-1 wet weight) in Callinectes Latimanus from Porto Novo lagoon

Hydrological Period	Tissue Type	Hg	Cd	Cu	Zn	Cr	Fe	Mn	Pd	Ni	Va	MH_3Hg
JULY-DEC 2014 (Rainy season)	GILL	0.002	0.032	10.46	16.50	61.96	150.41	13.30	137.33	10.18	0.00375	0.001
	Hepatop-ancreas	0.002	13.96	17.58	19.63	61.77	115.67	12.8	22.82	12.96	0.0065	0.001
	Carapace	ND	10.70	3.33	17.73	63.53	3.21	22.60	36.70	17.45	ND	ND
	GUT	0.002	14.63	4.09	37.64	15.90	62.07	17.17	18.84	9.44	0.0038	0.001
	MUSCLE	0.001	0.01	5.12	43.03	25.92	16.17	38.5	21.93	10.41	0.004	0.0003
	Total	**0.007**	**39.332**	**40.58**	**134.53**	**229.08**	**347.53**	**104.37**	**237.62**	**60.44**	**0.0185**	**0.0033**
	Mean (± SD)	0.001±0.001^{d}	7.87± 7.31^{cd}	8.12± 5.98^{cd}	45.82± 23.02^{abc}	45.82 ±23.02 ^{abc}	69.51± 63.19^{a}	20.87± 10.61^{bcd}	47.52± 50.67^{ab}	12.09±3.28^{bcd}	0.004± 0.002^{d}	0.001± 0.0005^{d}
JAN-JUNE 2015 (Dry season)	GILL	0.001	0.0007	1.00	2.75	1.81	164.58	9.86	70.30	3.80	0.0009	0.0003
	Hepatop-ancreas	0.0012	2.33	2.93	3.27	10.29	19.28	2.13	2.16	0.32	0.00011	0.00029
	Carapace	ND	0.02	0.42	4.43	0.31	12.88	9.98	5.40	0.03	ND	ND
	GUT	0.0011	0.01	3.15	6.27	3.70	255.21	216.25	19.97	0.13	0.00192	0.000271
	MUSCLE	0.001	0.013	5.28	7.17	9.20	731.1	38.40	300.46	**ND**	0.00217	0.00015
	Total	**0.0043**	**2.3737**	**12.78**	**23.89**	**25.31**	**1183.05**	**276.62**	**398.29**	**4.3**	**0.00439**	**0.001011**
	Mean (± SD)	0.001±0.0005^{b}	0.47± 1.04^{b}	2.56± 1.93^{b}	5.06± 4.46^{b}	5.06± 4.46^{b}	236.61± 294.68^{a}	55.32± 91.02^{b}	79.66± 126.42^{b}	0.86± 1.65^{b}	0.001± 0.0009^{b}	0.0002± 0.0002^{b}
WHO/FAO Limit (mg/day)		**0.5**	**0.1****	**3.0**	**60.0**	**50**	**43.0**	**2.0-9.0**		**0.214**	**0.5**	**0.0033**
USEPA Limit (mg kg-1)		**0.5**	**0.5**	**70**	**30**	**N/A**	**N/A**	**5.4**	**0.5**	**N/A**	**0.4**	**0.001**
EEC(mg kg-1)		**0.5**	**0.05**	**N/A**	**N/A**	**N/A**	**N/A**	**N/A**	**0.4**	**N/A**	**0.5**	**0.0016**
NRS (mg kg-1)		**0.5**	**N/A**	**0.5**	**N/A**	**N/A**	**N/A**	**N/A**	**0.5**	**N/A**	**N/A**	**0.0005**

N/A= Not Available

The concentration of trace metal pollutants in *Chrysichthys nigrodigitatus* and *Callinectes latimanus* may be due to position they occupied in the food web and their habitat in the aquatic environment. *Chrysichthys nigrodigitatus*, and Callinectes *latimanus* are demersal species that spend most of their life time in benthic sedimentation zones of lagoon ecosystem and the assorted natures of lagoon sediments gives it greater penchant to trap and settled a wide range of metal pollutants. However, *Chrysichthys nigrodigitatus* and *Callinectes latimanus* are omnivorous finfish and shellfish that feed on seeds, insects, bivalves (macro-invertebrates) and detritus this reiterate the findings of [10] on blue swimming crab and that of [14] on *Chrysichthys nigrodigitatus*. Feasting on these metal pollutants- laden macro-invertebrates and detritus bio-magnified the metal pollutants concentrations in the finfish and shellfish organs and tissues, this is in agreement with the citation of [3]. The gate way through which metal pollutants get settled and trapped in the sediments is through the flow of lagoon water with point source and non-point source pollution and since finfish and shell fish are aquatic animals that obtained oxygen for respiration through gills from dissolved oxygen in water, this perhaps may contribute to source of metal pollutants in their tissues and organs.

The inconsistency in the distribution of metal pollutants in the organs of *Chrysichthys nigrodigitatus* and Callinectes *latimanus* throughout the season can be attributed to sand mining by the local sand miners which cause upwelling of the sediment that are constantly re-distributing the metal pollutants in sediments. This is in agreement with the work of [11]. Also, spatial distribution of *Chrysichthys nigrodigitatus* and *Callinectes latimanus* in Porto-Novo Lagoon complex ecosystem with the attendant assorted natures of the sediments that are metal pollutants sedimentation selective [7] could also be responsible for the inconsistency. The seasonal variation of salinity in the complex of Porto-Novo Lagoon ecosystem, being the freshwater- brackish aquatic habitat could encourage the abundance or scarcity of some salinity- sensitive macro-invertebrates that form major food basis for *Chrysichthys nigrodigitatus* and *Callinectes latimanus.* The ingestion of these metal pollutants- laden macro-invertebrates during the seasonal period of abundance would bio-accumulate metal pollutants in higher concentration in the tissues of the finfish and shellfish than during the seasonal period of scarcity. However, different macro-invertebrates bio-accumulate different metal pollutants. This agrees with the finding of [10]. The concentration of any metal pollutants in the tissue may be a result of the type of macro-invertebrates and detritus *Chrysichthys nigrodigitatus* and Callinectes *latimanus* feed on, the size, age and the physiological need of the fish could also be responsible for varying degree of metal pollutants concentrations in different tissue of fish as published by [16].

Biomineralization of different organs/ tissues in finfish and shellfish in which living organisms produce minerals often to harden or stiffen existing tissues [12] could also be responsible for the disparity and inconsistency of metal pollutants detected in the tissues and organs of *Chrysichthys nigrodigitatus* and *Callinectes latimanus*, This also depends on the physiological need of the shell and fin fishes. Some metals are essential for specific dynamic activities in the body of animals but when the concentration exceeds the trace amount it becomes toxic for the animals and human consumption. The biological effect of metal pollutants in Porto-Novo Lagoon ranges from beneficial stimulation to harmful retardation and death in aquatic animals; this could be manifested in a number of ways as stated by [6]. Bio-accumulation of these metal pollutants can also pose health problems in human society in a recognizable food chains. Perhaps, the most celebrated case of metal pollutants poisoning in human population that led to Minamata disease outbreak was in Japan as cited by [6].

The recommended daily intake of all the metal pollutants investigated for human consumption is above FAO/ WHO limit for finfish and shellfish (Tables 1 and 2). The concentrations of metal pollutants in the edible parts of *Chrysichthys nigrodigitatus* and *Callinectes latimanus* in Porto-Novo lagoon ecosystem are not safe for consumption based on USFDA and EU regulation limit. The sources of these metal pollutants are from gutter, sewage, waste water from surrounding cities such as Cotonou, Abomey-Calavi, So-Ava; Also, urban concentrations of population due to increased urbanization, anthropogenic activities and garbage deposits along the Porto-Novo lagoon banks. [21].

IV. Conclusion and Recommendation

Analytical Laboratory Analysis using AAS and Exploratory Data Analysis revealed that all tested metal pollutants are present in quantifiable measurements in *Chrysichthys nigrodigitatus* and *Callinectes latimanus* from Porto-Novo lagoon ecosystem and they are above International standard permissible limits that could have lethal effect on *Chrysichthys nigrodigitatus* and *Callinectes latimanus* and human beings. It is therefore recommendation that Porto-Novo Lagoon should be put on National Priority List (NPL) for adequate environmental revamping and protection.

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