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ORIGINAL RESEARCH

Heavy-Metals Accumulation in Five Demersal Marine Species from Nigerian Coastal Waters (Eastern Central Atlantic, FAO Area 34)

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Abstract:
Introduction: Studies have shown that the extent of accumulation of heavy metals in fish is dependent on the metal types, fish species, and tissues. Heavy-metals accumulation in five demersal marine species from the Nigerian coastal water (FAO, Area 34) was investigated.
Aims: Assessing the bio-integrity and safety of *Parapenaeopsis Atlantica, Penaeus Monodon, Penaeus Notialis, Portunus Validus, and Cynoglossus Browni* from Lat N 60 28' 24", Long E 30 22' 50" from Nigeria water.
Materials and Methods: Five hundred and six specimens were sampled from 32 fishing trawlers and assessed for heavy metals concentration using 210 Atomic Absorption Spectrophotometer (AAS).
Results: The weight of *P. atlantica, P. monodon, P. notialis, P. validus and C. browni* were: 9.42 ± 0.26, 96.79 ± 2.38, 26.82 ± 1.34, 284.09 ± 7.34 and $411.09 \pm 15.27g$ respectively. Heavy-metal accumulated in the muscles (mg/kg) were: Lead (0.15 ± 0.05; 0.19 ± 0.06; 0.15 ± 0.02; 0.14 ± 0.07; and 0.14 ± 0.08) respectively, Iron (2.7 ± 0.07, 2.26 ± 0.06, 2.32 ± 0.08, 2.43 ± 0.12, and 2.42 ± 0.09) respectively, and Zinc (8.68 ± 0.12, 8.97 ± 0.14, 9.13 ± 0.12, 8.99 ± 0.11 and 8.86 ± 0.08) respectively.
Conclusion: Zn and Fe concentration in *P. Atlantica* were above the acceptable limit by FAO/WHO standard. The detection of lead, iron, and zinc in the muscles of species indicates the unsafe conditions for fishes. Regulatory agencies thus need to notify the public and enforce existing preventive laws, for the protection of lives.
Keywords: Fish species, marine water, heavy metals, tolerance limit

All co-authors agreed to have their names listed as authors.

1. INTRODUCTION

The Nigerian multispecies demersal stocks are exploited in great abundance. Demersal fishes (flounders, halibuts, soles, cods, hakes, haddocks, and miscellaneous demersal) contributed 12% of the total catches in 2009 (10.9 million tons), compared with almost 26% in the 1950s and 1970s [1]. Catches of crustaceans (crabs, lobsters, shrimps, prawns, krill, etc.) contributed 6% (5.4 million tons) in 2009, slightly lower than 7% in 2002. Molluscs (abalones, conchs, oysters, mussels, scallops, clams, squids, octopus, etc.) increased slightly from 6% in the 1950s and 1970s to 7% (6.2 million tons) in 2009 [2].
There are two main ways by which heavy metals enter the aquatic food chain. One is by direct consumption of these metals via water and food and non-dietary routes across permeable membranes such as the muscles and gills. Therefore, levels in fish usually reflect levels found in sediments and water of the particular aquatic environment from which they are sourced and time of exposure [3]. Fish can accumulate heavy metals in their tissues by absorption along the gill surface and kidney, liver, and gut tract wall to higher levels than environmental concentration. Accumulation of heavy metals by organisms may be passive or selective; and differences in the assimilation of heavy metals by organisms could be a result of differences in assimilation, ingestion, or both. Non-essential heavy metals such as Cadmium (Cd), Mercury (Hg), and Lead (Pb) have no known essential role in living organisms. They exhibit extreme toxicity even at very low (metal) exposure levels and have been regarded as the main threat to all forms of life, especially human health. Entry of heavy metals into the organs of a fish mainly takes place by adsorption and absorption; the rate of accumulation is a function of uptake and depuration rates [4].

Research has shown that the extent of accumulation of heavy metals in fish is dependent on the metal types, fish species, and tissues respectively. Water chemistry directly affects the accumulation of heavy metals in fish. Sediments are also known as an important factor of heavy metal accumulation in fish as it is considered as the major source of contaminants for bottom-dwelling and bottom-fed aquatic organisms, which in turn represents the concentrated source of metals in the diet of fish [5]. The aquatic organisms are sensitive to heavy metals when the concentrations of the metals reach a significant level in the water and sediment [6]. This is especially so in the case of crabs and shrimps because invertebrates tend to accumulate more metals than fish as a result of differences in the evolutionary strategies adopted by various phyla. Metals that are accumulated in crustaceans could be biomagnified in the food chain and ultimately affect human beings. Heavy metals are an important group of chemical pollutants, that mainly get into the human body through food. Some heavy metals are irreversibly bound to human body tissues e.g., cadmium to kidneys, and lead to bones [3]. The contaminants also concentrate in some of the organs of fish and can cause lethal and a range of sub-lethal effects. Fishes are often seen at the top of the aquatic food chain and may accumulate large amounts of heavy metals from their environment [7].

Fish that are relatively situated at the bottom of the aquatic food chain can accumulate heavy metals from food, water, and sediments. The content of toxic heavy metals in fish can counteract their beneficial effects. Several adverse effects of heavy metals on human health have been reported. This may include serious threats like renal failure, liver damage, cardiovascular diseases, and even death. Therefore, many international monitoring programs have been established to assess the quality of fish for human consumption and to monitor the health of the aquatic ecosystem [8].

In the last few decades, the concentrations of heavy metals in fish have been extensively studied in different parts of the world. Most of these studies concentrated mainly on the heavy metals in the edible part (fish muscles). However, other studies reported the distribution of metals in different organs like the liver, kidneys, heart, gonads, bone, digestive tract, and brain. El-Moselhy *et al;* [4] opined that metal bioaccumulation in fish and subsequent distribution in organs is greatly inter-specific. In addition, many factors can influence metal uptakes like sex, age, size, reproductive cycle, swimming patterns, feeding behaviour, and living environment. The specific objective of this study was to determine the heavy metals accumulation present in the tissues of the demersal fish species. The need to know the public health significance of heavy metals pollution present in Nigerian coastal waters cannot be over-emphasized, knowing well that the fish and crustaceans under study are exported and consumed locally.

STUDY AREA

The Nigerian Coastal waters fall within Eastern Central Atlantic FAO Area 34. The country is bordered to the North by the Republic of Niger and Chad, to the West by the Republic of Benin, to the East by the Republic of Cameroon and to the South by the Atlantic Ocean and with a coastline of approximately 853km facing the Atlantic Ocean. These coastlines lie between latitude $4^0 10^1$ to 6^0 20^1 N and longitude 2^0 45^1 to 8^0 35^1 E. The terrestrial portion of this zone is about 28,000km in area, while the surface area of the continental shelf is 46,300km [9]. The Coastal line has eight states it shares borders with. They are Lagos, Ogun, Ondo, Rivers, Delta, Akwa-Ibom, Bayelsa, and Cross River States. A trawler voyage of about fifty (50) days to and fro covers the area and also the eight coastal states.

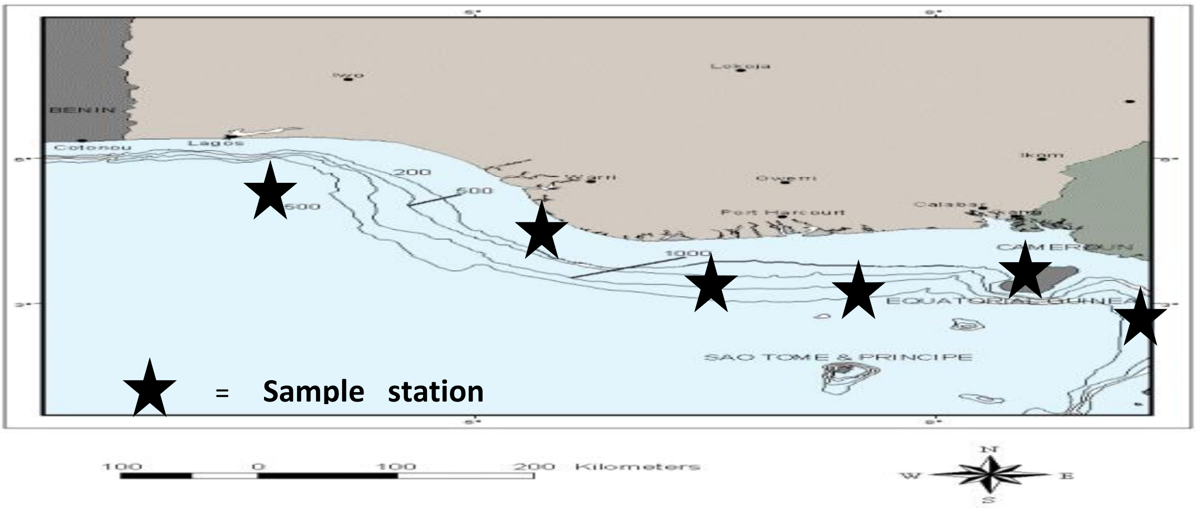

Figure 1: **Map showing Nigerian Coastal waters FAO Area 34** Source: [8]

2. MATERIAL AND METHODS

2.1. COLLECTION OF SAMPLES

Deep frozen samples (-20^{0}C) of *Cynoglossus Browni* (Nigerian tongue sole), *Parapenaeopsis Atlantica* (Brown Shrimp), *Penaeus Notialis* (White Shrimps), *Penaeus monodon* (Black tiger Shrimps), and *Portunus Validus* (Smooth Swim Crab) were obtained from 32 fishing trawlers owned by a private fishing company. A total of 506 samples of each species for a period of 6 months collected were thawed. Total length (TL), Standard length (SL), Head length (HL), Carapace length (CL), Body depth (BD) were measured with a measuring ruler taken to the nearest 0.1cm as well as the weight of each sample was recorded.

2.2. DETERMINATION OF HEAVY METALS

Tissue samples weighing 1.0g of twenty (20) specimens of each species were crushed into fine powder. They were then placed in 25ml conical flasks. 10ml of water was added to each and afterward 3ml of concentrated hydrochloric acid (HCl) was added. They were digested with 5ml concentrated nitric acid (HNO_3) and swirled to mix. The mixture was boiled on a hot plate. Water was continuously added to the mixture as it dries off. The mixture was smelt to ensure the acid was burnt off completely. Distilled water was then added to make it up to 100ml [10]. The completely digested sample was filtered and results were read using 210 Atomic Absorption Spectrophotometer (AAS) which uses acetylene gas in its operation. Different lamps were inserted to read the corresponding heavy metals in the sample. Metals such as Lead (Pb), Iron (Fe), Zinc (Zn), Arsenic (As), Mercury (Hg), and Cadmium (Cd) were detected and results were recorded in mg/kg unit [11].

2.3. STATISTICAL ANALYSIS

All data collected were subjected to one-way Analysis of Variance (ANOVA) using SPSS version 23, Game-Howell's post HOC tests were used because data were heterogeneous invariances. A Levine's test was conducted for homogeneity.

3. RESULTS AND DISCUSSION

.3.1 MORPHOMETRIC CHARACTERISTICS

This study investigated five demersal species (*Parapenaeopsis Atlantica, Penaeus monodon, Penaeus Notialis*, *Portunus Validus*, and *Cynoglossus Browni*) from the Nigerian coastal water (FAO, Area 34) to assess the bio-integrity and safety of these kinds of seafood for export. Five (5) morphometric characters were taken into account, except for *P. Validus* that was exempted from both total length (TL) and standard length (SL), similar to the report of Seralathan *et al;* [12] who investigated the relationship between fifteen morphometric characters of *P. monodon* of cultured and wild species. Species used for this present work were all from the wild and samples were collected in a deep-frozen state and then thawed to enable accurate readings. In a similar study off Lagos Coast by Lawal-Are *et al;* [13] on *Portunus Validus*, after examining 618 specimens reported the weight to be from 82.3g to 694.0g while in this present study, the weight of the 506 specimens of *Portunus Validus* ranged from 130g to 450g. The morphometric characters were subjected to the Game-Howell's post HOC test since the observations were heterogeneous invariances. This showed that *P. Atlantica* and *P. Notialis* showed similar mean values only for their carapace length while both species showed statistically different observations for other variables. All species had significantly different results for other variables.

The results as shown in Tables 1 and 2, presents mean and standard deviation/error values of morphometric characteristics of the five different species considered. *P. Atlantica* was observed to have the least average mean body depth of 1.17cm and weight of 9.42g, which is closely followed by *P. Notialis (2.08)*. *C. Browni* was observed to have the highest body depth (10.23) and a mean total weight of 411.08g.

3.2 HEAVY-METALS

Six heavy metals in five demersal species which include: *Parapenaeopsis Atlantica, Penaeus notialis, Penaeus monodon*, *Portunus Validus*, and *Cynoglossus Browni* were investigated in this study. These metals were lead (Pb), zinc (Zn), iron (Fe), arsenic (As), cadmium (Cd), and mercury (Hg). The results of heavy metals in the five species are shown in table 3. *P. Atlantica* contained a mean Pb concentration of 0.15±0.02, Fe 2.7±0.32, and Zn 8.68±0.5. *P. Monodon* contained Pb of 0.19±0.06, Fe 2.26±0.06, and Zn 8.91±0.51; similar to *P. Notialis, C. Browni,* and *P. Validus.* The result also revealed that As and Cd were less than 0.01 for all the species; and Hg was not detected (ND). Figure 4 shows that Zn composition had similar average distribution in all species studied. Also, the same distribution pattern was observed for Pb and Fe in Figures 5 and 6 respectively.

Table 1: **Morphometric measures, Condition factors and Regression Analysis of Examined fish species from the Nigerian Coastal waters**

Species	Mean Total Length (cm)	Mean Total Weigl (g)	Range (Total Length)	Mean condition Factor (K)	Regression Constant (a)	Regressio Coefficient (b) slope	Correlatio Coefficient (r)
Parapenaeopsis atlantica	11.56	9.42	8.6 - 14.1	0.605	-11.69	1.83	0.74
Penaeus notialis	14.71	26.82	10 - 19.2	0.77	-49.23	5.17	0.95
Penaeus monodon	22.55	96.79	17.7 - 27.8	0.834	-14.78	10.84	0.77
Portunus Validus	14.77	284.09	11.1 - 17.8	8.77	-29.8	39.42	0.75
Cynoglossus Browni	46.32	411.09	36.9 - 64.3	0.412	-54.87	20.72	0.7

Table 2: Games-Howell Post Hoc Test for the Morphometric characteristics

Parameter	*P. Atlantica*	*P. monodon*	*P. Notialis*	*C. Browni*	*P. Validus*
Carapace length (cm)	5.19[a]	8.37[b]	5.22[a]	7.66[c]	14.77[d]
Body depth (cm)	1.17[a]	3.38[b]	2.08[c]	10.23[d]	6.96[e]
Weight (g)	9.42[a]	96.79[b]	26.82[c]	411.09[d]	284.09[e]
Total length (cm)	11.56[a]	22.55[b]	14.71[c]	46.32[d]	-
Standard length (cm)	9.91[a]	18.68[b]	12.09[c]	42.84[d]	-

Note: The same row with different superscripts shows results are significantly different at p<0.05

Table 3: Mean (±SD) concentration of Heavy metals(mg/kg) in muscles of fish species collected from Nigerian coastal waters.

Fish species	Lead (Pb)	Iron (Fe)	Zinc (Zn)	Arsenic (As)	Mercury (Hg)	Cadmium (Cd)
P. Atlantica	0.15±0.02 (0.11 – 0.19)	2.7±0.32 (2.11 – 3.18)	8.68±0.55 (7.38 – 9.44)	<0.01	ND	<0.01
P. monodon	12±0.03 (0.1 – 0.2)	26±0.29 96 – 3.14)	8.97±0.51 (8.1 – 9.66)	<0.01	ND	<0.01
P. notialis	15±0.09 (0.1 – 0.5)	23±0.36 96 – 3.24)	9.13±0.52 (7.81 – 9.63)	<0.01	ND	<0.01
C. browni	14±0.03 (0.1 – 0.21)	43±0.45 01 – 3.97)	8.99±0.48 (8.06 – 9.87)	<0.01	ND	<0.01
P. validus	14±0.04 (0.1 – 0.22)	42±0.39 97 – 3.5)	8.85±0.38 (7.85 – 9.47)	<0.01	ND	<0.01

Note: Heavy-metals is in mg/kg, Data in mean ±SD, Range in parenthesis, ND means Not Detected.

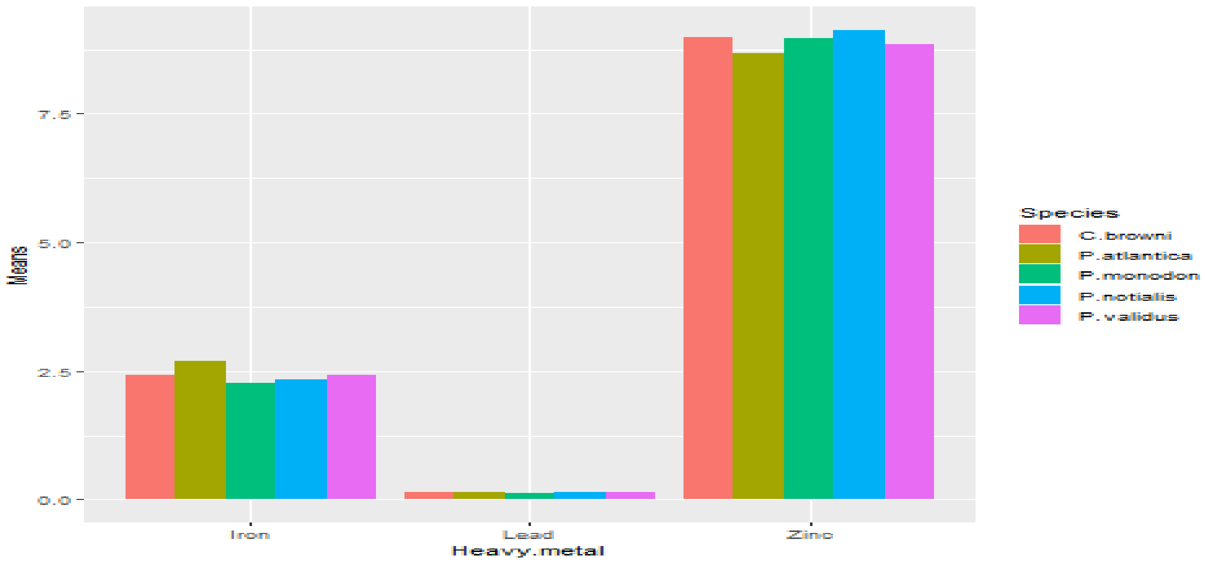

Figure 2: Heavy metal contents in the species studied

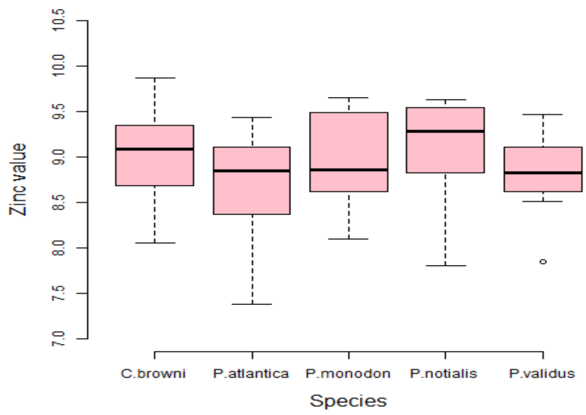

Figure 3: Zinc composition in all species

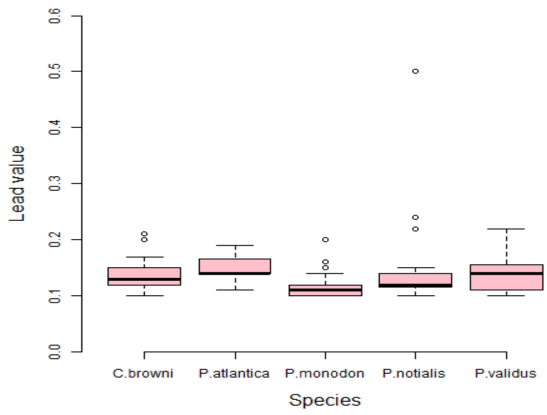

Figure 4: Lead composition in all species

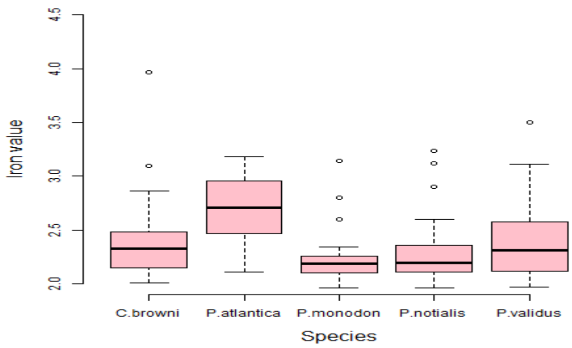

Figure 5: Iron composition in all species

Table 4: Turkey's HSD Post HOC test for Heavy Metals Accumulation and FAO/WHO limits

Heavy metal (mg/Kg)	Species					**FAO/WHO Limits**
	P. Atlantica	*P. Monodon*	*P. Notialis*	*C. Browni*	*P. validus*	
Lead (Pb)	0.15 ± 0.05[a]	0.19 ± 0.06[a]	0.51 ± 0.02[a]	0.14 ± 0.07[a]	0.14 ± 0.08[a]	0.3
Iron (Fe)	*2.7 ±0.07[a]	2.26 ± 0.06[b]	2.34 ± 0.08[b]	2.43 ± 0.12[b]	2.45 ± 0.09[b]	2.5
Zinc (Zn)	*8.68 ± 0.23[a]	*8.91 ± 0.14[a]	*9.19 ± 0.16[a]	*8.97 ± 0.19[a]	*8.85 ± 0.08[a]	1.0
Arsenic (As)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.0
Cadmium (Cd)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.0
Mercury (Hg)	ND	ND	ND	ND	ND	

*Note: Same superscripts along the row indicate means are not significantly different at p-value =0.05**

Heavy metals pollution has been linked to the cause of massive death of fishes and this has been attributed to human-related pollution activities which were based on land. Industrial and domestic waste usually contain heavy metals such as cadmium, iron, zinc, copper, etc, which found their way into drainages and onward transfer to the marine water bodies. Several scientists have pointed out that heavy metals have several deleterious negative impacts on aquatic species, other mammals, and human beings. The main sources of these are batteries, galvanized pipes, fertilizers, sewage sludge, and plastics. Such may be the cause of accumulated heavy metals found in the muscles of the species under study from the FAO, Area 34 of the Nigerian marine water.

It is suggested that benthic fish are likely to have higher heavy metal concentrations than fish inhabiting the upper water column because they are in direct contact with the sediments and their greater uptake of heavy metal concentrations from zoo-benthic predators. Zhao *et al;* [14] found that *Cynoglossus Gracilis* had the lowest level of metal accumulation among investigated species despite being a typical benthic fish. El-Moselhy *et al;* [4] reported weak support for this, where variations between pelagic and benthic organisms were detected and only a high concentration of iron (Fe) in the gills of the benthic fish *Synodontis sp.* were detected.

Summary of the observations made on the five species is shown in Table 1 and a grouped bar chart in Figure 2, for the mean content of Iron, Zinc, and Lead for the species in this study. However, Hg was not detected (ND) in any of the species, while Arsenic and Cadmium Cd were detected at low concentrations. All the species were observed to contain Pb, Fe, and Zn in different proportions; analysis of variance was used to ascertain the similarities of the Iron, Lead, and Zinc composition in species. The order of the mean concentration analysed in the muscles of the Species was Zn>Fe>Pb. The uniformity in the distribution observed in the five species showed that the composition of Iron and Zinc were uniformly spread in the species, while lead was not uniformly spread for all the species. Further study was done, to determine the species' significant disparities using Turkey's HSD Post Hoc Test (Table 4). The distribution of metals was statistically different as shown in table 4; *P. Atlantica* contained higher Fe (2.7±0.32) concentration than *P. Monodon* (2.26±0.29) and *P. Notialis* (0.23±0.36), (2.43±0.45) in *C. Browni,* and 2.42±0.39 in *P. Validus*. These tests were all conducted at the 95% confidence interval. However, Zn was highest in *P. Notialis* (9.13±0.52), and lowest in *P. Atlantica* with 8.68±0.55mg/kg. Lead was not significantly different in all species with an average mean value of 0.15mg/kg.

However, this present study did not put into account pelagic or mid-water species but the highest heavy metal in the demersal species was observed in Zn for *P. Notialis* (9.13mg/kg). The Zn values for all species considered in this study exceeded the FAO/WHO limit of 1.0mg/Kg. However, the mean Iron content for all the five species was within the FAO/WHO limit except for *P. Atlantica* (Table 3) which is slightly above the 2.5mg/Kg limit of FAO/WHO. In a study by Prabhu et al; [6], it was discovered that the mean concentration of metals in *P. monodon* was Pb>Fe>Cd>Zn>Cu>Cr in pre-monsoon and Pb>Fe>Zn>Cd>Cu>Cr in post-monsoon. Also, Emmanuel *et al;* [15] revealed that heavy metals in males *Portunus Validus* have a decreasing concentration of metals in the following order of Fe>Cr>Zn>Cu>Cd>Co>Pb. While in this present study, the order of the mean concentration analysed in the muscles of the Species was Zn>Fe>Pb. As and Cd had relatively very low values of <0.01, while Hg was not detected in all samples. An analysis of variance test on the mean values of the heavy metals showed no significant different result observed for Pb and Zn (in Table 4) for the five species. However, Fe was significantly ($P<0.05$) higher in *P. Atlantica* than other species.

This research is of great significance and timely in the light of the recent occurrence of massive dead croaker fishes creating an uproar in the Niger Delta regions of the Nigeria waters which forced the regulatory agencies to launch investigations into the cause of the development. But the agencies reported in their findings that the toxins could have emanated from land-based sources which were usually emptied into the water. The Director-General of the National Oil Spills Detection and Response Agency (NOSDRA) in a statement [16, 17] insisted the toxicity found in the dead fishes was caused by pollution from heavy metals from industrial and domestic wastes. Other agencies involved in the investigation were the Nigerian Maritime Administration and Safety Agency (NIMASA) and the Nigerian Institute of Oceanography and Marine Research (NIOMR) amongst others.

4.0 CONCLUSION

The levels of Zn and Fe in P.atlantica were above acceptable limits by FAO/WHO standard of 1.0 and 2.5 mg/l respectively. The decreasing order of mean concentrations was Zn>Fe>Pb. Arsenic (As) and Cadmium (Cd) concentration were less than 0.01 for all the species. Mercury (Hg) was not detected in all the species. The detection of lead, iron, and zinc in the muscles of species under study indicates the unsafe conditions of the fish species. Regulatory agencies thus need to notify the public and enforce existing preventive laws, for the protection of lives.

COMPETING INTEREST

The authors declare that there is no conflict of interest.

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