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Heavy metals concentrations in four selected seafood from crude oil polluted waters of Ogoniland, Rivers State, Nigeria

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ABSTRACT

This study was carried out to determine the concentrations of heavy metals (cadmium, chromium, zinc, manganese, lead and iron) in some fish speciesand crustaceans collected from Kaa, B-Dere and Bodo City in Ogoniland, Rivers State, Nigeria. A Total of two types of fish species and crustaceans were investigated. They were analyzed with atomic absorption spectrophotometer (AAS). The highest level of 1520 ± 1.62 of iron was recorded in Penaeus notialis from Bodo City while Liza falcipinis from Kaa shows the least value of 290 ± 0.97. Maximum concentration of manganese was recorded in Tilapia queneensis and the minimum value was recorded in Liza falcipinis. High levels of chromium, cadmium, lead and zinc were recorded in Tilapia queneensis, Callinectes pali, Penaeus notialis and Tilapia queneensis respectively. Liza falcipinis had the least concentrationsofcromium, cadmium andzinc while Penaeus notialis had the least concentrations of lead. All the fish speciesand crustaceans collected from the sites contained detectable amounts of the elements investigated. It was observed that the level of heavy metals in all the fish species werehigh except for chromium detected in Tilapia queneensis, Liza falcipinis, Callinectes pali and Penaeus notialis which was lower than the permissible limits for human consumption designated by the USEPA, WHO, and FAO. The present study shows that precaution measures need to be taken as the levels of heavy metals detected in seafood from these sites posed serious threat to the populace that feed on them. It also improves the baseline data and information on chromium, lead, cadmium, zinc, manganese and iron concentrations in saltwater fishes and crustaceans (Tilapia queneensis, Liza falcipinis, Callinectes pali and Penaeus notialis) commonly marketed in OgoniLand. Such data provide valuable information on safety of fishes commonly consumed by the public.

Keywords: *Tilapia queneensis, Liza falcipinis, Callinectes pali, Penaeus notialis***,** Heavy Metals, Ogoniland.

INTRODUCTION

Heavy metals pose a great concern to the Scientists as they cause environmental contamination by exhibiting behaviors consistent with those persistent toxic chemicals. The heavy metals cannot be degraded further, and their toxic effects can be long lasting, unlike the organic contaminants that decompose into other chemicals with time [1]. Heavy metals are known to have toxic effects even at low concentration, and their concentration in biota can be increased through bio-accumulations [2].The importance of biodiversity has been increasingly considered for the cleanup of metal contaminated and polluted ecosystems. This subject is emerging as a cutting edge area of research gaining commercial significance in the contemporary field of environmental biotechnology [3].

Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulation in the ecosystem, agriculture, and human body has received widespread attention in recent years [4]. It obvious that organisms vary significantly in their responses to environmental hazardous substances. In some circumstances substances that are perceived to be vital for continuous existence of some living things, may be extremely poisonous to others. A typical example is oxygen which is believed to be vital for life is toxic to some anaerobic bacteria [5]. Certain substances are known to be environmentally heinous when they are pose a substantial or hazard to human health, including other living things. Such substances often times are lethal, non-degradable and persistent in nature and can be biologically magnified or cause detrimental cumulative effects [6].

The use of fish and invertebrates as bio indicators of water quality has been advocated by several workers [7,8]. This is because they produce evidence of relatively stable concentration compared with water analysis that indicates only short term conditions. A considerable amount of studies have been carried out on the effects of pollution in Nigerian water bodies. Victor and Tetteh [9] reported a reduction in fish diversity associated with discharge of municipal wastes and industrial pollutants into the Ikpoba River, while [10] investigated heavy metal concentration in some dominant fish in the river and found that the fish species showed higher mean levels, with variable contamination factor and bioaccumulation quotient among stations.

Fish accumulate toxic chemicals such as heavy metals directly from water and diet, and contaminant residues may ultimately reach concentrations hundreds or thousands of times above those measured in the water, sediment and food [11,12,13]. Heavy metals are normal constituents of marine environment that occur as a result of pollution principally due to the discharge of untreated wastes into rivers by many industries.

Bioaccumulation of heavy metals in tissues of marine organisms has been identified as an indirect measure of the abundance and availability of metals in the marine environment [14]. For this reason, monitoring fish tissue contamination serves an important function as an early warning indicator of sediment contamination or related water quality problems [15,16] and enables us to take appropriate action to protect public health and the environment. Multiple factors including season, physical and chemical properties of water can play a significant role in metal accumulation in different fish tissues. Several studies [17,18,19,20,21] have also indicated that fish are able to accumulate and retain heavy metals from their environment depending upon exposure concentration and duration as well as salinity, temperature, hardness and metabolism of the animals. Adeyeye [22] also showed that the concentration of metals was a function of fish species as it accumulates more in some fish species than others.

Exposure to toxic metals is associated with many chronic diseases. As per available report, when metallic toxicant finds their way into the body, there are possible mechanisms through which they act. Some of which are:

(a) Inhibition of Enzymatic Activities: This is so because some metals such as Pb, Hg and Cd have affinity for sulphur and therefore attack sulphur bonds in enzyme, thus immobilizing them. Other site of attack include the free amino (-NH2) and carboxyl (-COOH) groups in protein [23].

(b) Attacks on Cell Membrane and Receptor: The heavy metals bind to cell membrane and receptor, thereby altering their structures. This affect transport and other inter or intra cellular processes in the body. Cd inhibits oxidative phosphorylation in the body [23].

(c) Interference with Metabolic Cations: Heavy metals interfere with the metabolism of essential cations such as absorption, transportation, decomposition and storage. Cd follows the pathway of Zn and Cu metabolisms. Pb replaces Ca in bones [23].

(d) Action on the Artery: Heavy metals can increase the acidity of the blood. The body draws Ca from the bones to help restore blood pH. Further toxic metals set up conditions that lead to inflammation in arteries and tissues, causing more Ca to be drawn to the area as a buffer. The Ca, coats the inflamed area in the blood vessel but creating another by the hardening of the artery walls and its progressive blockage of the arteries. This leads to osteoporosis [23].

The present study was undertaken to study the concentration levels of selected heavy metals in commercially important fish species and its human health implications.

MATERIALS AND METHODS

2.1 Study area

Ogoniland has a tragic history of pollution from oil spills and oil well fires; although no systematic scientific information has been available about the ensuing contamination. Ogoniland is a region covering some 1,000 km2 in the south-east of the Niger Delta basin (**Figure 1**). It has a population of close to 832,000, consisting mainly of the Ogoni people.

Figure 1.0: Map of Ogoniland showing the two Local Government Areas (LGA) were the study was carried out (Khana and Gokana, LGA).

2.2 Collection of test samples

Fresh samples of four selected important aquatic fauna *Tilapia queneesis* (tilapia), *Liza falcipinis* (mullets), *Callinectes pali* (crabs) *and Penaeus notialis* (shrimps), were collected from landing beaches of Ogoni communities namely; Bodo City, B-Dere and Kaa water side in Gokana and Khana Local Government Areas (LGA) of Rivers State, Nigeria. The identities of the aquatic sample were confirmed at the Hydrobiology Unit, Department of Animal and Environmental Biology, University of Port Harcourt, Nigeria. At each site, ten individual fishes, crabs and shrimps of similar size of each species were collected, cleaned and wrapped in aluminum foils, then kept frozen in an ice chest before transported to the laboratory for analysis.

2.3 Reagents

All reagents used in this study were of analytical grades with high purity.

2.3.0 Determination of Heavy Metals levels in fishes, crabs and shrimps
2.3.1 Processing
The samples was oven dried for three days for thorough drying, after that it was grounded to powder form using silimic mortar. 5 grams of the sample was weighed into a crucible container, and then introduced into a furnace to derive the ash for 6 hours. After 6 hours, a crucible thug was used to carry out the crucible from the furnace into a desiccator and allowed to cool. After cooling, 5ml of 10% HCL was used to dissolved or warm the ash content to near dryness. After that, it was filtered into a funnel and measuring cylinder and made up to 20ml with distilled water for the metal analysis using atomic absorption spectroscopy.

2.3.2 Atomic Absorption Spectroscopy Analysis
For each of the metals, atomic absorption spectroscopy was calibrated using standard of the metals, which are given below as Cr (λ) = 357.90nm, Cd (λ) = 228.80nm, Pb (λ) = 283.30nm, Zn (λ) = 213.9nm, Mn (λ) =279.50nm, Fe (λ) = nm). 5 grams of the samples was digested in 20ml 10% hydrochloric acid (HCL) on a heating mantle to near dryness. Cr, Zn, Mn and were analyzed using Hollow Cathode Lamp (HCL) in a Flame atomizer AAS. Cd and Pb were analyzed using Electrode Less Discharge Lamp (EDL) in the Flame atomizer AAS. The extract was aspirated directly into the atomic absorption spectroscopy machine.

2.3.3 Atomic Absorption Spectroscopy Conditions
The atomic absorption spectroscopy (AAS) was GBC Avanta pm ver 2.02 Avanta. The carrier gas was acetylene and air: 70psi. In order to analyze a sample for its atomic constituents, the samples were atomized. The atomizer used was flames atomizers. The atoms was then be irradiated by optical radiation, and the radiation source was an element-specific line radiation source. The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector.

RESULTS

The average Heavy Metals concentrations (above mean ± S.E.M, mg/kg wet wt.) in *Tilapia queneensis,Liza falcipinis*, *Callinectes pali and Penaeus notialis* are shown in **Table 1, 2, 3** and **4**. A total of six heavy metals were analyzed for, namely: chromium (Cr), cadmium (Cd), lead (Pb), zinc (Zn), manganese (Mn) and iron (Fe).All the samples collected from the three sites contained detectable amounts of the elements studied. These elements were present in the entire fish sample and at varying concentrations. It must be noted that, varying concentrations of the heavy metals were measured in *Tilapia queneensis, Liza falcipinis*, *Callinectes pali and Penaeus notialis* with some fishesreporting very high concentrations whilst other samples measured relatively lower concentrations of the elements. With Iron tended to be the highest concentration in all the samples investigatedas compared to other elements measured from the three sites. Concentrations of Manganese in *Tilapia queneensis* varied from 52.9 ± 0.08 to 61.2 ± 0.11 mg/Kg (dry wt) while Iron recordedwere 627 ± 1.89, 860 ± 0.99 and 1079 ± 4.33 mg/Kg (dry wt.) from Kaa, B-Dere and Bodo City, respectively. Similarly concentrations of Zinc were ranged from 28.7 ± 0.12 to 45.5 ± 0.28 mg/Kg (dry wt.) while that of Lead were 12.9 ± 0.11, 16.2 ± 0.13 and 15.7 ± 0.31 mg/Kg (dry wt.) from Kaa, B-Dere and Bodo City, respectively. Among all the heavy metals analyzed for, chromium and cadmium were the lowest but not below WHO permissible limits. Their concentrations from the three sites are as follows; 0.64 ± 0.00, 0.77 ± 0.01 and 0.97 ± 0.01 for Cadmium and 3.72 ± 0.07, 5.63 ± 0.08 and 9.97 ± 0.1 mg/Kg (dry wt.) for Chromium recorded in*Tilapia queneensis* collected from Kaa, B-Dere and Bodo City.

Also, concentrations of Zinc recorded in *Liza falcipinis* varied from 22.5 ± 0.20 to 32.1±0.09 mg/Kg (dry wt.) while Iron ranged from 290± 0.97 to 1037± 1.01 mg/Kg (dry wt.), with iron recorded in *Liza falcipinis* from B-Dere having the maximum concentrations of iron recorded in *Liza falcipinis*. Similarly, concentrations of Manganese were ranged from 8.63±0.20 to 11.8±0.06 mg/Kg (dry wt.) while that of Lead were 10.1± 0.18, 7.45±3.67 and 9.98±0.01 mg/Kg (dry wt.) collected from Kaa, B-Dere and Bodo City respectively. Also, concentrations of Zinc recorded in *Callinectes pali* were 31.4±0.12, 42.6± 0.66 and 30.8±0.11 mg/Kg (dry wt.) collected from Kaa, B-Dere and Bodo City, respectively while Iron concentrations measured were 857±0.12, 1038±1.09 and 1285±2.74 mg/Kg (dry wt.) from Kaa, B-Dere and Bodo City respectively. Similarly, concentrations of Lead were ranged from 20.9±0.27 to 27.2±0.05 mg/Kg (dry wt.) while that of Manganese recorded were 38.9±0.57, 27.6±0.03 and 15.5±0.16 mg/Kg (dry wt.) from Kaa, B-Dere and Bodo City respectively with *Callinectes pali* collectedfrom Kaa having the highest concentrations.

Table 1: Heavy metals concentrations (mean ± S.E.M, mg/kg wet wt.) in *Tilapia queneensis* from the study areas (Kaa, B-Dere and Bodo City)

Heavy Metals	Kaa	B-Dere	Bodo City
Cr	3.72 ± 0.07^{a}	5.63 ± 0.08^{b}	9.97 ± 0.10^{c}
Cd	0.64 ± 0.00^{a}	0.77 ± 0.01^{a}	0.97 ± 0.01^{a}
Pb	12.9 ± 0.11^{a}	16.2 ± 0.13^{b}	15.7 ± 0.31^{c}
Zn	28.7 ± 0.12^{a}	45.5 ± 0.28^{b}	31.1 ± 0.33^{c}
Mn	55.4 ± 0.24^{a}	52.9 ± 0.08^{b}	61.2 ± 0.11^{c}
Fe	627 ± 1.89^{a}	860 ± 0.99^{b}	1079 ± 4.33^{c}

Value are expressed as mean ±standard error of mea n (SEM) of three replicates, (n=3). Values with different superscript letters (a, b, c) in the same column are significantly different at the 0.05 level (P≤0.05)

Table 2: Heavy metals concentrations (mean ± S.E.M, mg/kg wet wt.) in *Liza falcipinis* from the study areas (Kaa, B-Dere and Bodo City)

Heavy Metals	Kaa	B-Dere	Bodo City
Cr	1.94± 0.08 ^{a}	6.18 ± 0.08^{b}	6.78 ± 0.02^{b}
Cd	0.50 ± 0.00^{a}	1.48 ± 0.01^{b}	0.85 ± 0.01^{a}
Pb	10.1 ± 0.18^{a}	7.45 ±3.67^{b}	9.99 ± 0.01^{a}
Zn	22.5 ± 0.20^{a}	25.8 ± 0.47^{b}	32.1± 0.09^{c}
Mn	9.83 ± 0.13^{a}	8.63 ± 0.19^{b}	11.8 ± 0.06^{c}
Fe	290 ± 0.97^{a}	1037 ± 1.01^{b}	760 ± 4.62^{c}

Value are expressed as mean ±standard error of mea n (SEM) of three replicates, (n=3). Values with different superscript letters (a, b, c) in the same column are significantly different at the 0.05 level (P≤0.05)

Table 3: Heavy metals concentrations (mean ± S.E.M, mg/kg wet wt.) in *Penaeus notialis* from the study areas (Kaa, B-Dere and Bodo City).

Heavy Metals	Kaa	B-Dere	Bodo City
Cr	2.92 ± 0.03^{a}	4.84 ± 0.04^{b}	6.52 ± 0.09^{c}
Cd	0.86 ± 0.02^{a}	0.95 ± 0.04^{a}	1.38 ± 0.01^{b}
Pb	23.5 ± 0.35^{a}	30.6 ± 0.27^{b}	6.91 ± 0.06^{c}
Zn	30.8 ± 0.21^{a}	31.7 ± 0.07^{b}	34.3 ± 0.04^{c}
Mn	21.9 ± 0.76^{a}	24.7 ± 3.49^{b}	26.6 ± 0.29^{c}
Fe	1038 ± 1.37^{a}	1281 ± 1.24^{b}	1520 ± 1.62^{c}

Value are expressed as mean ±standard error of mea n (SEM) of three replicates, (n=3). Values with different superscript letters (a, b, c) in the same column are significantly different at the 0.05 level (P≤0.05).

Table 4: Heavy metals concentrations (mean ± S.E.M, mg/kg wet wt.) in *Callinectes pali* from the study areas (Kaa, B-Dere and Bodo City)

Heavy Metals	Kaa	B-Dere	Bodo City
Cr	3.77 ± 0.02^{a}	6.27 ± 0.05^{b}	4.18 ± 0.29^{a}
Cd	0.78 ± 0.01^{a}	1.79 ± 0.01^{b}	1.64 ± 0.39^{b}
Pb	20.9 ± 0.27^{a}	22.9 ± 0.08^{b}	27.2 ± 0.05^{c}
Zn	31.4 ± 0.12^{a}	42.6 ± 0.66^{b}	30.8 ± 0.11^{c}
Mn	38.9 ± 0.57 ^{a}	27.6 ± 0.03^{b}	15.5 ± 0.16^{c}
Fe	857 ± 0.12^{a}	1038 ± 1.10^{b}	1285 ± 2.74^{c}

Value are expressed as mean ±standard error of mea n (SEM) of three replicates, (n=3). Values with different superscript letters (a, b, c) in the same column are significantly different at the 0.05 level (P≤0.05)

DISCUSSION

Heavy metals concentration in fish species

Fish is widely consumed in many parts of the word by humans because it has high protein content, low saturated fat and also contains calcium, phosphorus, iron, trace elements like copper and a fair proportion of the B-vitamins known to support good health [24].Many reports on contamination of fish by chemicals in the environment were reported [25]. Heavy metals are considered the most important constituents of pollution from the aquatic environment and the sea due to toxicity and accumulation by marine organisms, such as fish [26,27].

All the aquatic samples collected from the sites contained detectable amounts of the elements studied (Cadmium, Chromium, Lead, Zinc, Manganese and Iron). These elements were present in all the fish samples and at varying concentrations. It must be noted that, varying concentrations of the heavy metals were measured in the sampled fishes with some fishes reporting very high concentrations whilst other samples measured relatively lower concentrations. Among the different metals analyzed Cadmium and Chromium are classified as chemical hazards and maximum residual have been prescribed for human [28,29]. Cadmium and chromium tended to be the least concentrated in the fish as compared to other elements measured. Concentrations of cadmium varied from 0.50± 0.01 to 1.79±0.01 mg/Kg (dry wt.) which is high compared to the permissible level of 0.01 mg/Kg. The greatest sources of zinc in humans are sea foods and meats [30]. Exposure to heavy metals such as cadmium and chromium is of immediate environmental concern. A direct relationship between heavy metal poisoning and thyroid dysfunction was reported in rabbits by Ghosh and Bhattacharya [31]. Concentrations of Zinc in the fish samples were relatively high (22.5± 0.20 to 45.5 ± 0.28 mg/Kg), the maximum value was recorded for *Tilapia queneensis* collected from B-Dere, which is higher than the permissible level of 5 mg/Kg. Chromium ranged between 1.94±0.08 to 9.97±0.09 mg/Kg (dry wt.). The lowest was recorded for*Liza falcipinis* collected from Kaa and the highest was recorded for *Tilapia queneensis* collected from Bodo City respectively. The maximum permissible chromium level for fish is 102 mg/kg as reported by WHO [32]. This shows that chromium measured in all the aquatic samples were below FAO permissible level. Iron had the highest concentration among all the metals analyzed in this present study; it ranged between 290 ± 0.97 to 1520 ± 1.62 mg/Kg (dry wt.) which is 5,067 times higher than the permissible level of 0.30 mg/Kg by WHO and 3,040 times higher than the permissible levels of 0.5 mg/Kg by USEPA.

Results in **Table 1 - 4**showed that lead levels ranged from 6.91±0.06 to 30.6±0.27 from the three sites for *Penaeus notialis* collected from Body City and B-Dere respectively. The lead levels recorded in all the species exceeded the permissible limits of WHO [32] which mentioned that lead level should not be more than 2 mg/Kg. This study also showed that Manganese levels in all the test samples are high and above the permissible limits as recommended by WHO and USEPA (0.02 and 0.5 mg/Kg respectively). Humans that relay on the fish and water from OgoniLand are at great risk. The bioaccumulation of these metals may pose great hazard to health of humans.

Chronic lead poisoning is characterized by neurological defects, renal tubular dysfunction and anemia. Damage of Central Nervous System is a marked feature especially in children [33]. In men, lead affects the male gametes resulting in sperm abnormalities and decreased sexual desire as well as sterility [34]. In women, lead poisoning is associated with abnormal ovarian cycles and menstrual disorders in addition to spontaneous abortion [35].

In the present study, it was observed that the total concentration of iron in all the fish species and crustaceans studied was significantly higher when compared with that of cadmium ($P < 0.05$) and also significantly higher than chromium, manganese, zinc, lead, cadmium. Lead was significantly higher than chromium. It can be deduced from the above that accumulation of the heavy metals is more of species-related. In addition to this, it was noted that there was no relationship between the accumulation patterns of different metals in the different fishes.

The accumulation of metals by the fish depends on the location, feeding behavior, trophic level, age, size; duration of exposure to metals and homeostatic regulation activities of fish [36,37] has listed multiple factors that influence metals accumulation in fish such as season, physical and chemical properties of water. Knowledge of metals concentration in fish is important to management for various purposes such as risk of taking fish as part of diet and metals pollution control strategies. Most of fish are at top in aquatic food chain and have potential to accumulate high metals content even in mild polluted conditions. Therefore, metals concentration in fish could be used as an index to estimate level of pollution especially in aquatic bodies [38] even in the lake system.

This difference in the pattern of heavy metals distribution in the four fish species might be a result of their difference in many factors such as; feeding habits, habitats, ecological needs, metabolism, biology and physiology [39]. Generally, heavy metal uptake occurs mainly from water, food and sediment [40]. However, the efficiency of metal uptake from contaminated water and food may differ in relation to ecological needs, metabolism, and the contamination gradient of water, food and sediment, as well as other environmental factors such as salinity, temperature and interacting agents [41]. Several endemic fish species have become threatened [42] leading to the depletion of our fish resources and substantial reduction in their nutritive values [43]. Chemical analysis of fish, therefore, ensures dietary safety of the fish from a particular body of water [44]

Consequently, it can be concluded that the levels of heavy metals in these fish species are at unacceptable levels for all the studied samples in these sites. Only chromium in *Tilapia queneensis*, *Liza falcipinis*, *Callinectes pali* and *Penaeus notialis* were lower than the acceptable values for human consumption designated by the FAO, [28]. The present study shows that precaution measures need to be taken in order to prevent future heavy metal pollution. It also improves the base line data and information on chromium, lead, cadmium, zinc, manganese and ironconcentration in saltwater fish (*Tilapia queneensis*, *Liza falcipinis*, *Callinectes pali* and *Penaeus notialis*) commonly marketed in OgoniLand. Such data provide valuable information on safety of fishes commonly consumed by the public.

CONCLUSION

This study established the fact that heavy metals concentrations detected in *Tilapia queneensis*, *Liza falcipinis, Callinectes pali and Penaeus notialis* are high and, thus, consumption of these fishes may pose significant health risk to the populace who consume this fish species. A further comprehensive study of heavy metals and other contaminants in seafood in OgoniLand is recommended to better understand and control these pollutant in the OgoniLand coastal marine environment and to ascertain if these contamination levels of these heavy metals in seafood remain the same in the incoming years, because Ogoniland is constantly exposed to heavy metals contamination from oil spills as a result of increasing pipeline vandalism. The community should take a proactive and public stand against individuals or groups who engage in illegal activities such as bunkering and artisanal refining. These activities result in a huge environmental footprint, seriously impacting public health and livelihood activities, particularly fishing and agriculture.

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