Bio-Accumulation of Heavy Metals in Seafood from the Kaani River in the Ogoni Axis, Rivers State, Nigeria.

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Abstract
This work describes the bioaccumulation of heavy metals (Mn, Cr, Cu, Cd, Ni, Zn, Fe, As, and Pb) in seafood from the Kaani River in the Ogoni axis of Rivers State, Nigeria. The seafood examined were; shrimps, tilapia, mudskippers, and crabs. After a preliminary treatment and digestion with a combination of concentrated acids (HNO_3, HCl, and H_2SO_4) mixed in a 5:3:2 ratio in a steam bath. The trace metals in the sediments and seafood were examined separately. An atomic absorption spectrophotometer (AAS) was used to first measure the contaminants' concentrations in the matrix and seafood samples. Based on dry weight, the results ranged from 0.0037 to 0.0291 for Mn, NA to 1.0581 for Cd, 0.0025 to 0.0257 for Cu, 0.0005 to 0.0188 for Cr, 0.0054 to 0.2299 for Pb, 0.5142 to 1.0791 for Fe, 0.0914 to 1.1283 for Zn, 0.0.0847 to 1.6644 for As, and 0.0312 to 0.4422mg/kg for Ni. The bioaccumulation factor was calculated using the ratio of the trace element concentration in the seafood to that in the matrix. The analytical results indicated that the concentrations of each of these trace elements varied. The findings demonstrated that, with the exception of mudskipper (1.6644) and crab (1.0957) in stations 3 and 4, which demonstrate bioaccumulation for arsenic (As), seafood from various stations [(station 1 (Maa di binnise Igbara waterside), station 2 (Mann Stream), station 3 (Woman Stream), and station 4 (Nwii ke ma kor stream)] did not bio- accumulate any of the investigated trace metals. It was also discovered that the crab at station 4 bio-accumulated zinc (1.1283), iron (1.0791), and cadmium (Cd) (1.0581). When compared to the national and international needed targets, these findings clearly showed heavy metal accumulation in mudskipper and crab from various stations of the River, which indicated that ingestion of this particular creature signals a health threat. As a result, it is best to discourage the careless dumping of untreated garbage into bodies of water.

Keywords: *Bioaccumulation, Contaminants, Matrix, Treatment, Seafood*

Introduction: The uptake, storage, and accumulation of organic and inorganic pollutants by organisms from their surroundings is referred to as bioaccumulation. Thus, complicated interactions between different pathways of absorption, excretion, passive release, and metabolism lead to bioaccumulation. According to Nwineewii and Ibok (2014), fish undergo bioaccumulation through two different pathways: dietary absorption through the consumption of contaminated food particles, and aqueous uptake of chemicals present in water.

Bio-concentration is the portion of bioaccumulation that comes from aqueous exposure and is absorbed by the gills. Bio-magnification is the word used to describe the contribution of intestinal mucosa uptake, resulting from dietary exposure, to bioaccumulation. The different elimination methods are significant co-determinants for bioaccumulation in both scenarios (Murtala et al., 2012). Because they are abundant in mineral organic compounds and are not removed from aquatic ecosystems by natural processes like organic contaminants, metals are significant pollutants. The introduction of metallic pollutants into aquatic systems via sewage, effluents, and rubbish leaching results in significant harm to aquatic species (Heba, 2004).

It has long been known that heavy metals seriously harm the aquatic ecology. Aquatic creatures may be exposed to unusually high concentrations of heavy metals due to increased heavy metal flow into natural aquatic environments (Bhattacharya et al., 2007). Metals that enter the aquatic ecosystem may not directly harm organisms, but they can be deposited in aquatic organisms by the processes of bio-concentration, bioaccumulation, and other food chain processes. As a result, when humans consume seafood, the concentrations of these metals can be dangerous to human health (Jayaprakash et al., 2015).

Fish carry metals through their blood, where the ions are typically bonded to proteins. As a result of coming into contact with the fish's organs and tissue, the metals accumulate to varying degrees in various fish organs and tissues (Lakshmanan et al., 2009). After an aquatic creature accumulates heavy metals, they can pass through the upper echelon of the food chain (Gobas et al., 1999).

Seafood from contaminated areas poses a possible health risk to humans, despite being an essential part of human nutrition. Metals can linger in water and sediments and build up in aquatic species like fish. In a disturbed aquatic ecosystem, seafood are the straightforward and trustworthy biomarkers of metal contamination since they typically absorb these metals from their immediate surroundings (Klumpp et al., 2002). Thus, the purpose of this study was to evaluate the bio-accumulation of heavy metals in seafood from the Kaani River.

Materials and Methods.

An explanation of the research area: In Kaani, in the Ogoni axis of Rivers State, a freshwater local river served as the site of the inquiry. The area located on the Gulf of Guinea coast in Rivers State, east of Port Harcourt. It includes the Khana Local Government Areas and a large portion of Nigeria's Niger Delta. The geographic locations of the sample locations are displayed in Table 1.

Table 1. Geographic Positions of Sample Locations

River	Sample Identity	Location	Geographic Location (Coordinates)
Kaani.	1	Maa di binnise Igbara waterside	Lat. 4.6793^0N
Kaani.	2	Mann Stream	Long. 7.3809^0E
Kaani.	3	Woman Stream.	Lat. 4.6791^0N
Kaani	4	Nwii ke ma kor stream	Long. 7.3850^0E

Sample Collection and Preparation: During low tide, sediment samples were collected from several sites along the river using a plastic trowel and placed in a sterile container. The samples were delivered to the laboratory for analysis after being sealed in polythene bags to avoid contamination. Local fishermen used fishing gears to gather seafood from different areas that were being studied. The seafood was then brought to the laboratory in an ice cooler. The wet composite samples were dried in the laboratory by air separately until their weight remained constant. The materials were macerated in a ceramic mortar using a pestle and then sieved through a 0.2 mm mesh screen. Seafood samples and the associated powdered particles were kept in glass vials sealed tightly. Two grams (2g) of the dried material were digested using the method described by Nwajei et al. (2014), and the digest was then recovered by filtration.

Sample Analysis: The amounts of the heavy metals were subsequently determined by analyzing the digests using an atomic absorption spectrophotometer (AAS).

Model Assessments: By calculating the bioaccumulation factor of the seafood from the various areas under research, the bioaccumulation of heavy metals in seafood was determined. Using an atomic absorption spectrophotometric approach, the concentrations of the selected trace metals (Mn, Cr, Cu, Cd, Ni, Zn, Fe, As, and Pb) in seafood (shrimps, mudskipper, crab, and tilapia) and the matrix (sediments) were determined. Next, the concentration ratio was assessed using the method outlined by Mansour & Sidky (2002) and Hiller et al. (2009).

Results and Discussion.

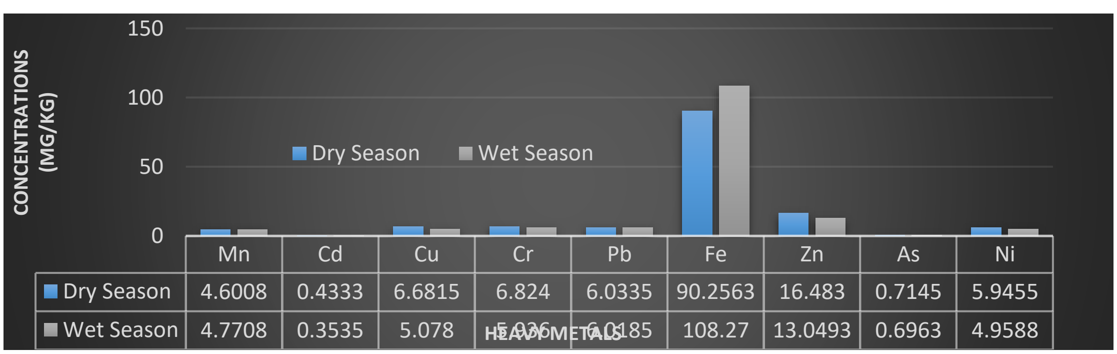

Fig 1: The average difference in heavy metal contents between the dry and wet seasons in Kaani River Seafood samples.

Table 2: The average concentrations of heavy metals in seafood samples collected from several sites along the Kaani River.

Heavy metals (mg/Kg)	Seafood				Mean±SD	FAO/WHO limit
	Shrimp	Tilapia	Mudskipper	Crab		
Mn	0.0493±0.068	0.0285±0.209	0.0164±0.298	0.0801±0.192	0.0436± 0.092	0.5
Cd	0.0090±0.005	0.0520±0.006	0.0730±0.013	0.0783 ±0.060	0.0531±0.021	0.05
Cu	0.0156±0.199	0.0367±0.211	0.0651±0.132	0.1346±0.239	0.0630±0.195	0.05
Cr	0.0621±0.484	0.0029±0.213	0.1544±0.489	0.0327±0.160	0.0630±0.337	0.06
Pb	0.6420±0.195	0.4160±0.408	0.0524±0.250	1.4780±0.455	0.6471±0.327	0.3
Fe	73.1930±2.758	88.6150±3.607	104.0080±5.114	131.2370±3.720	99.2633±3.799	100
Zn	13.7350±0.822	12.1300±1.060	16.4950±1.327	16.7060±1.663	14.7670±1.218	100
As	0.0350±0.003	0.0842±0.054	0.1215±0.019	0.1030±0.472	0.0859±0.137	0.05
Ni	0.2280±0.316	1.3230±0.406	1.0010±0.099	2.2580±0.339	1.2025±0.290	0.6

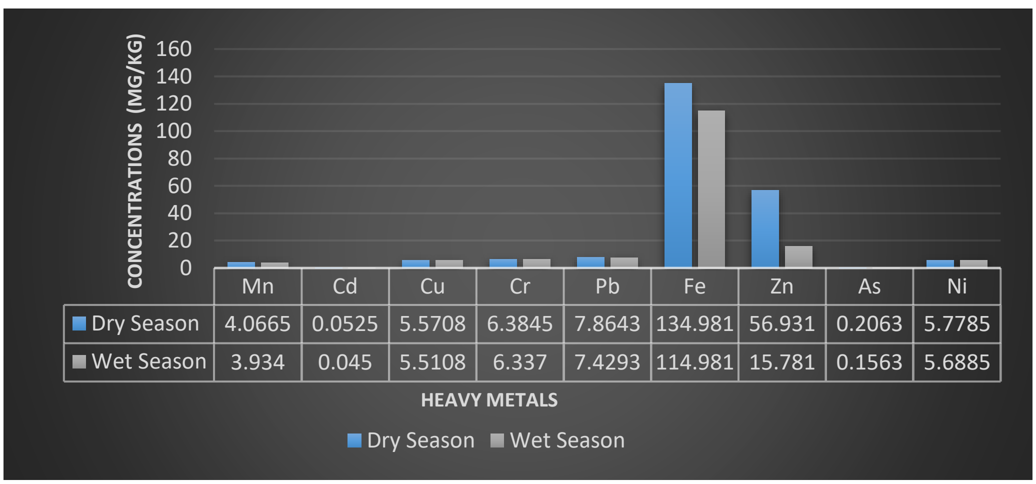

Fig 2: The Kaani River sediment's mean fluctuation in heavy metal contents during the dry and wet seasons.

Table 3: The average concentration of sediment samples collected from the Kaani River at various stations.

Heavy metals (mg/Kg)	Stations				Mean±SD	DPR Limit	WASV
	1	2	3	4			
Mn	5.362±0.054	3.675±0.007	4.316±0.011	2.648±0.011	4.000 ± 0.021	850	850
Cd	NA	0.126±0.000	0.000±0.001	0.069±0.005	0.049±0.002	0.8	0.3
Cu	6.154±0.014	6.164±0.049	4.666± 0.010	5.179± 0.212	5.541±0.071	36	45
Cr	5.372±0.217	5.377±0.012	8.166±0.018	6.361± 0.074	6.361± 0.074	100	90
Pb	7.403±0.053	7.383±0.028	9.474±0.198	6.327±0.046	7.647±0.081	85	20
Fe	137.348±3.226	132.348±2.505	118.613±2.683	111.614±2.278	124.981±2.673	38T	47T
Zn	16.118±0.356	16.118±0.291	98.481±5.619	14.707±0.106	36.356±1.593	140	120
As	0.363±0.001	0.196±0.001	0.073±0.004	0.094±0.003	0.182±0.002	13	10
Ni	7.212±0.038	4.423±0.003	6.243±0.019	5.056±0.034	5.734±0.024	35	68

WASV (World Average Shale value) of sediment, 2002.
NA (Not Available)

Table 4: Bioaccumulation Factor (BF) of heavy metals in seafood samples.

Heavy metals	Seafood			
	1 Shrimps	2 Tilapia	3 Mudskipper	4 Crab
Mn	0.0091	0.0077	0.0037	0.0291
Cd	NA	0.3824	NA	1.0581
Cu	0.0025	0.0059	0.0138	0.0257
Cr	0.0115	0.0005	0.0188	0.0050
Pb	0.0839	0.0544	0.0054	0.2299
Fe	0.5142	0.6225	0.7784	1.0791
Zn	0.8469	0.7479	0.0914	1.1283
As	0.0847	0.3437	1.6644	1.0957
Ni	0.0312	0.2981	0.1599	0.4422

NA (Not Available)

Table 5: Interpretation of intervals of Bioaccumulation Factor (BF)

Classification of BF	Bioaccumulation Level
BF > 1	Implies Bioaccumulation
BF = 1	Implies Bio-indication
0 <BF< 1	No Bioaccumulation
BF = 0	Not Available
BF < 0	Not Available

Murtala et al., (2012)

$$BF = \frac{concentrations\ of\ heavy\ metals\ in\ seafood\ (\frac{mg}{kg})}{\text{concentrations of heavy metals in sediment } (\frac{\text{mg}}{\text{kg}})}$$

Table 2 shows the findings for the average concentration of heavy metals in seafood samples from the Kaani River at various sites. The mean concentrations of Mn and Cd in the stations during the course of the year vary from 0.0164±0.298 to 0.0801±0.192 mg/kg, with a mean value of 0.0436± 0.092 mg/kg and 0.0090±0.005 to 0.0783±0.060 mg/kg and 0.0531±0.021 mg/kg, respectively; Cu lie within the range of 0.0156±0.199 to 0.1346±0.239 mg/kg within the stations with a mean value of 0.0630±0.195 mg/kg; Cr lie within the range of 0.0029±0.213 to 0.1544±0.489 mg/kg within the stations with a mean value of 0.0630±0.337 mg/kg; Pb lie within the range of 0.0524±0.250 to 1.4780±0.455 mg/kg within the stations with a mean value of 0.6471±0.327 mg/kg; Fe lie within the range of 73.193±2.758 to 131.237±3.720 mg/kg within the stations with a mean value of 99.263±3.799 mg/kg; Zn lie within the range of 12.130±1.060 to 16.706±1.663 mg/kg within the stations with a mean value of 14.767±1.218 mg/kg; As lie within the range of 0.0350±0.003 to 0.1215±0.019 mg/kg within the stations with a mean value of 0.0859±0.137 mg/kg and Ni lie within the range of 0.2280±0.316 to 2.2580±0.339 mg/kg within the stations with a mean value of 1.2025±0.290 mg/kg respectively.
The result recorded for the mean concentration of sediment samples from Kaani River at the different stations is presented in Table 3. The mean concentration of Mn within the year lie within the range of 2.648±0.011 to 5.362±0.054 mg/kg within the stations with a mean value of 4.000 ± 0.021mg/kg; Cd lie within the range of 0.000±0.000 to 0.126±0.000 mg/kg within the stations with a mean value of 0.049±0.002 mg/kg; Cu lie within the range of 4.666± 0.010 to 6.154±0.014 mg/kg within the stations with a mean value of 5.541±0.071 mg/kg; Cr lie within the range of 5.372±0.217 to 8.166±0.018 mg/kg within the stations with a mean value of 6.361± 0.074 mg/kg; Pb lie within the range of 6.327±0.046 to 9.474±0.198 mg/kg within the stations with a mean value of 7.647±0.081 mg/kg; Fe lie within the range of 111.614±2.278 to 137.348±3.226 mg/kg within the stations with a mean value of 124.981±2.673 mg/kg; Zn lie within the range of 14.707±0.106 to 98.481±5.619 mg/kg within the stations with a mean value of 36.356±1.593 mg/kg; As lie within the range of 0.073±0.004 to 0.363±0.001 mg/kg within the stations with a mean value of

0.182±0.002 mg/kg and Ni lie within the range of 4.423±0.003 to 7.212±0.038 mg/kg within the stations with a mean value of 5.734±0.024 mg/kg respectively.
Tables 4 present the findings of the investigation on the bioaccumulation of heavy metals in seafood samples from various Kaani River stations. The seafood samples that were subjected to analysis included crab (Callinectes gladiator), mudskipper (Periophthalmus barbarus), tilapia (Tilapia sparrmani), and shrimp (Penaeus monodon). The bioaccumulation factors was calculated using the ratio of concentration of pollutants in the seafood to that in sediment. Dry weight was the basis for variation in the results. All of the seafood (shrimps, tilapia, crab, and mudskipper) in the sampled stations (1-4) showed zero bioaccumulation for Mn, Cu, Cr, Pb, and Ni when the results were applied to the classification intervals provided by Murtala et al. (2012) (table 3). This is because all of the stations' heavy metal bioaccumulation factors fell into the category of BF < 1, which denotes no bioaccumulation. With the exception of crab at station 4, where the bioaccumulation factor of Cd was larger than 1, indicating bioaccumulation, the results obtained for Cd indicated that no heavy metal was being bio-accumulated by any seafood. With the exception of station 4, where the bioaccumulation factor of Fe was more than 1, indicating that the crab was bio-accumulating Fe, shrimp, tilapia, and mudskipper had zero bioaccumulation of Fe.
With the exception of station 4, where crab bio-accumulated zinc because station 4's zinc bioaccumulation factor was larger than 1, suggesting bioaccumulation, the values obtained for zinc in stations 1, 2, and 3 were less than 1, showing no bioaccumulation of zinc by shrimp, tilapia, and mudskipper. Since the bioaccumulation factor of As in stations 3 and 4 was greater than 1, mudskippers and crabs bio-accumulated As there, but shrimp and tilapia did not bio-accumulate in stations 1 or 2. The results of this study are consistent with those of Nwineewii and Ibok (2014), whose research on Penaeusmonodon (Shrimps) revealed different levels of bioaccumulation by the seafood and indicated that ingesting the organism foretells health risks. The results of Wokoma (2014) on the bioaccumulation of trace metals in water, sediments, and crab from the Sombreiro River in the Niger Delta are similarly consistent with our findings.

It has been observed that fish can absorb metals from water through their skin, gills, and oral intake. The incapacity of the fish to metabolize the heavy metals or the metabolism of the heavy metals in the fish tissues may have contributed to the bioaccumulation of heavy metals in mudskippers (Periophthalmus spp) (Sirot et al., 2009).
Over the past ten years, there has been evidence of heavy metal bioaccumulation, particularly cadmium, in aquatic animals (Jayaprakash et al. 2015). The bioaccumulation of arsenic may be connected to the high concentration of the element in mudskipper tissue. Klumpp et al. (202I) also reported a similar outcome. This may lead to death of the fish and general loss of aquatic diversity (Bhattacharya et al. 2007).

Conclusion

This study examined the quality of seafood exposed to home and agricultural effluent in terms of heavy metal and microbiological contamination. The quantities of heavy metals found in fish and crab are not high enough to have an immediate negative impact on health, but long-term exposure to fish through protracted bioaccumulation may result in chronic health problems. The general population should be made aware of the potential for health issues resulting from eating fish tainted with dangerous bacteria and heavy metals.

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