

Low levels of heavy metals in shrimps (*Decapoda: Atyidae*) from Omodo River in southern Nigeria

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Abstract

Shrimps remain an important source of proteins worldwide. The contamination of the environments with effluence such as from domestic, healthcare systems, industrial waste discharges and agricultural run-offs; are posing much danger to the consumption of shrimp diets by humans in particular. The ingestion of heavy metals from sediment and in water column is chiefly the source of contamination to the shrimps. This study was conducted quarterly and spanned from December, 2012 to May, 2014 with the objectives to determining the background levels of eight heavy metals in whole body mass of crustacean (*Caridina africana* and *C. gabonesis*) as well as in the sediments. Standard methods were employed in the sampling and analyses. The results obtained for heavy metals in sediments were in folds higher than what were obtained in the shrimps tissues. The mean range of concentrations of metals in the sediment across the stations were in the order; Zn (15.076-18.182 mg kg⁻¹) > Cu (6.146-8.130 mg kg⁻¹) > Pb (0.131-0.198 mg Kg⁻¹) > Co (0.033-0.045 mg kg⁻¹) > Cr (0.017-0.028 mg kg⁻¹) > Cd (0.002-0.010 mg kg⁻¹) > Ni (0.003-0.008 mg kg⁻¹) > V (0.001 mg kg⁻¹). The values of heavy metals in shrimps as obtained in this study were far below the limit stipulated by Food and Agricultural Organisation (FAO) and have indeed confirmed the non-industrial waste disposal into the water bodies in Agbiede-wetlands including Omodo River.

Keywords: Analysis; Agbiede; concentrations; ingestion; sediment; shrimps.

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Introduction

Bioavailability or bioaccumulation of metals is a reflection of the amount ingested or the amount biologically available for ingestion in free form by the organism. While bioaccumulation describes the distribution among the different tissues and the extent to which the metal is retained in each tissue type (Murugan *et al*, 2008).

Aquatic organisms are bathed in solutions that contain metals and therefore, they may take up metals directly in their dissolved form. In a water environment, metals are potentially accumulated in the sediments and animals, and subsequently transferred along the food chain to humans (Firat *et al*, 2008; Mortuza and Al-Misned, 2017). Marine and freshwater crustaceans can be used as bioindicators of environmental pollution since they can accumulate these metals and other pollutants (Protasowicki *et al* 2013). Crayfish are suitable bioindicators of the xenobiotics in freshwater ecosystems due to their rapid bioaccumulation and long retention times. Heavy metals, also referred to as non-essential metals, are not considered as playing any significant role in the metabolism. Mercury, lead and cadmium are known to be extremely toxic even at

relatively low concentrations. Thus metals can accumulate in water, sediment or organic tissues through physicochemical or biological processes (Pinheiro *et al*, 2013).

It was reported that industrial discharges as well as domestic and healthcare sources containing toxic and hazardous substances, including heavy metals are the major factors contributing tremendously to the pollution of the aquatic ecosystem (Gbem *et al*, 2001; Woodling *et al*, 2001).

Amirah *et al* (2013) stated that in the aquatic environment heavy metals are easily taken up by aquatic organisms where they are strongly bound with sulfhydryl groups of proteins and accumulate in their tissues. The accumulation of heavy metals in the tissues of organisms can result in chronic illness and cause potential damage to the population. Heavy metal intake by aquatic organisms in a polluted aquatic environment is dependent on ecological requirements, metabolism and other factors such as salinity, water pollution level, and food and sediment quality. All heavy metals are potentially harmful to most organisms at some level of exposure and absorption (Yilmaz, 2003; Enuneku *et al*, 2014).



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Murugan *et al* (2008) studied the bioaccumulation pattern of Zn in freshwater fish (*Channa punctatus*) after chronic exposure. They realized that there was a significant difference ($p < 0.05$) in liver, kidney, intestine and gill not occurring only in muscle.

The analyses of the study carried out by Stanek *et al* (2014) revealed that the mean metals concentrations ($\text{mg}\text{Å}^{-1}\text{kg}^{-1}$) in the meat of the crayfish and in the exoskeleton were in the following order; Zn (115.571) > Mn (18.825) > Cu (17.226) > Ni (15.472) > Pb (3.535) > Cr (0.769) > Co (0.551) > Cd (0.315) > Hg (0.138) and (Mn (111.640) > Zn (11.355) > Ni (8.165) > Pb (6.695) > Co (0.595) > Cu (0.575) > Cd (0.379) > Cr (0.195) > Hg (0.0168)), respectively. These values were considered low when compared to some study else in the tropics and temperate regions of the world.

Comparatively, Obasohan and Eguavon (2008) examined the seasonal variations of bioaccumulation of heavy metals in a freshwater fish (*Erpetoichthys calabaricus*) from Ogba River, Benin City, Nigeria. The aim was to assess and monitor the accumulation of heavy metals level like; Cu, Mn, Zn, Ni and Pb in the fish. The level of mean values of Cu, Mn and Ni in fish for both wet and dry seasons exceeded WHO limit.

This study is the very first of a kind to be carried out within and around Agbede Town in southern Nigeria, which is an agrarian town and popular for its wetlands. Hence, the aim was to ascertain the healthiness of the crustaceans consumed by humans upon harvest from Omodo River by analysing for the levels of heavy metals in sediments and crustacean species (whole tissues) across three sampled stations along the river stretch. Therefore, this material is a rich baseline document for subsequent studies within and around the domain.

Materials and methods

The study-area

Omodo River which lies within longitude ($06^{\circ}16.3''\text{E}$, $06^{\circ}18.7''\text{E}$) and latitude ($06^{\circ}52.2''\text{N}$, $06^{\circ}55.4''\text{N}$) flows in the East direction, with few tributaries of seasonal streams. It is a tributary of Edion River and eventually empties into the lower Niger River (Figure 1). The description of the study area have been published in previous studies (Olomukoro and Dirisu, 2014; and Dirisu and Olomukoro, 2015).

Station 1 is located just by the confluence between Omodo River and Egwavo Stream, accessible through Ayuele Secondary School. The topography is characteristically a steep v-valley with lots of erosional streams when it rains and there is a dense canopy cover from the *Bambusa* thickets (*Bambusa* sp). All forms of human activities which include; bathing, washing of clothes, fermentation of cassava for starch and fishing take place here. On the banks are major agricultural activities like cassava farms, and plantations which include; Duca nut trees, plantain (*Musa* sp) and Cashew trees (*Anacardium occidentale*) which are occasionally treated with herbicides during weed control.

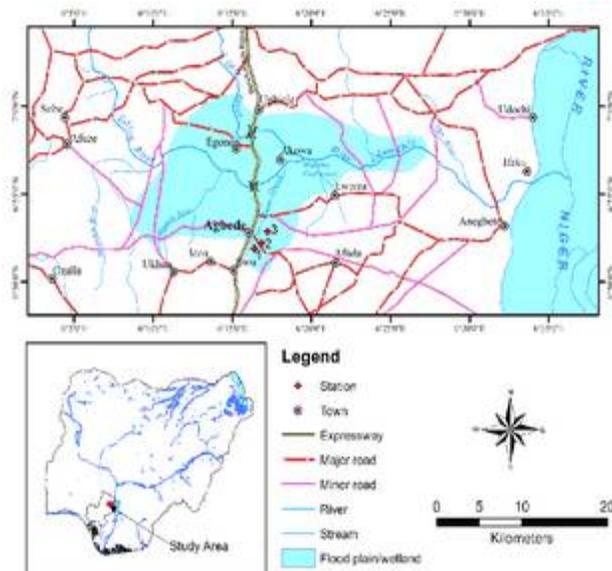


Figure 1. Map of the study-area in Agbede Wetlands.

Station 2 is located at Odighie Village by the bridge linking Agbede and Ama/Idegun towns which is over 1.5 km from Station 1. There is even more canopy cover by *Bambusa* sp. Washing of auto-bikes, bathing and washing of clothes are the major human impacts here. It serves over four communities within Agbede.

Station 3 is located about 1.2 km from Station 2 and the last sampling point on the River stretch which is located by the bridge at Egho Village unto Rabho-Imes farms land. It is the major source of water for every form of activity by the various Fulani, Igbo and other Etsako-speaking tribes farm Camps. Nomadic activities are very high here and consequently there are always litters of cattle faecal matter in the water and on the river banks.

Determination of heavy metals in sediment

Heavy metals in sediment were determined in the laboratory using the total open digestion method (APHA, 2005). 1 g of air dried sediment was passed through a 2 mm sieve with foil paper and was transferred into a 250 ml conical flask. A measured volume of well-mixed acids; perchloric acid, nitric acid and sulphuric acid in the ratio 1:2:2 was transferred into the flask containing the sediment sample in a fume hood. The content was heated on the hot plate for about 20 minutes until white fumes were observed emanating from the conical flask. The digestion process was stopped immediately and the sample was allowed to cool. Distilled water (about 20 mL) was added after cooling and boiled to gently bring the metals into solution. The filtrate was passively strained through Whatman's 42 filter paper into a 100 ml volumetric flask, and the heavy metal and the heavy metals of the filtrate was then determined for Cadmium, Zinc, Iron, Copper, Lead, Manganese, Nickel and Chromium using the *Thermo Jarrel Ash* Atomic Absorption Spectrophotometer (Series, 2782, model 757) in mgkg^{-1} .

Bioaccumulation study in crustaceans (shrimps)

Whole body mass of identified shrimp species (*C. africana* and *C. gabonensis*), collected from three stations at three months intervals (between December, 2012 and March, 2014) by using the methods for sampling macrobenthic fauna (Olomukoro and Dirisu, 2014). Consequent on collection, specimens were kept in vial bottles wrapped in foil papers, and kept at low temperature not >20°C (in a cooler containing ice). They were then transferred to the laboratory. Whole body mass were digested completely in a solution of well mixed nitric acid, sulphuric acid and perchlorate acid (in the ratio 2:2:1) using the open digestion method in the laboratory (Olowu *et al*, 2010) and the extracted solution upon digestion was there after ran in an AAS analyser (thermo jarrel ash series) to determine the levels of heavy metals of interest (Cadmium, Zinc, Iron, Copper, Lead, Manganese, Nickel and Chromium) measured in mg kg⁻¹. Quality assurance and control were adhered to both in the field and laboratory (APHA, 2005).

Data analysis of results

Basic measurement of central tendency including one-way analysis of variance (ANOVA) was used for the analysis of data. Graphs were plotted using Microsoft Excel tool for graphics.

Results

The analysis of the mean, minimum and maximum concentration values of heavy metals in sediments of Omodo River across the sampled stations in mgkg⁻¹ is presented in Table 1. Of all the eight metals investigated, only Iron (Fe) had high mean values ranging between 206.32 and 343.59 mgkg⁻¹ at stations 3 and 1 respectively.

Meanwhile, relatively low concentrations were recorded for Cr, Ni and Pb (values <5 mgkg⁻¹). A high significant difference was only observed for the means of Mn ($p>0.001$) amongst the metals across the stations and the seasons.

Bioaccumulation study of heavy metals in the whole body mass of shrimps (*Caridina africana* and *C. gabonensis*) from the lotic ecosystem (Omodo River) is presented in Table 2 and Figure 2. Eight heavy metals were analysed (copper, zinc, cadmium, vanadium, chromium, nickel, lead and cobalt) in the crustaceans (*C. africana* and *C. gabonensis*) and the results showed that there was statistically a significant difference on the temporal and spatial concentration in values across the stations ($p<0.05$).

The concentrations of heavy metals in shrimps were far below what was recorded for sediments. Copper mean concentrations across the stations (Station 1 to 3) ranged between 6.146 mgkg⁻¹ at station 2 to 8.139 mgkg⁻¹ at Station 3. The monthly variations ranged between 5.02 mgkg⁻¹ at Station 2 and 9.524 mgkg⁻¹ at Station 3. The means were significantly differed from one another ($p<0.05$). Zinc which did not differed significantly ($p>0.05$) from one station to the other, had its mean concentrations between a low of 16.530 and a high of 18.182 mgkg⁻¹ at Stations 1 and 3 respectively. The temporal variations ranged from 15.076 mgkg⁻¹ at Station 2 to 19.025 mgkg⁻¹ at the same Station 2 across the seasons.

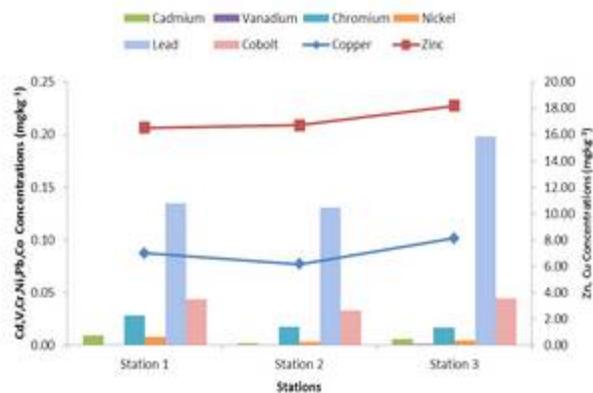
Cadmium had its mean concentrations between 0.002 mgkg⁻¹ at Station 2 and 0.010 mgkg⁻¹ at Station 1. There was a high significant difference ($p<0.01$) amongst the tested means. Vanadium mean values did not statistically vary from station to station. The mean concentrations stood at 0.001 mgkg⁻¹ at all the stations. Meanwhile, the minimum and maximum values were between BDL and 0.001 mgkg⁻¹.

Table 1. Summary of the mean, minimum and maximum physicochemical characteristic values in sediment of the study area from December, 2012 to May, 2014.

Parameters	Unit	Station 1	Station 2	Station 3	p-value
		$\bar{x} \pm SD$ (Min-Max)	$\bar{x} \pm SD$ (Min-Max)	$\bar{x} \pm SD$ (Min-Max)	
Iron	mgkg ⁻¹	343.59±367.11 (91.51-1050.56)	234.93±151.43 (101.24-588.96)	206.32±78.34 (91.33-423.43)	0.06
Zinc	mgkg ⁻¹	34.63±25.34 (12.21-72.29)	33.95±22.46 (13.19-63.01)	32.30±23.40 (10.18-60.22)	0.10
Copper	mgkg ⁻¹	24.94±12.89 (9.11-43.75)	32.38±26.66 (9.07-89.00)	28.82±21.48 (8.15-66.15)	0.45
Manganese	mgkg ⁻¹	52.20 ^{ab} ±25.95 (21.21-93.11)	37.47 ^c ±10.03 (20.46-44.75)	46.85 ^{bc} ±11.27 (33.33-60.62)	0.00
Cadmium	mgkg ⁻¹	8.44±7.20 (0.22-16.51)	9.45±8.07 (0.31-21.37)	9.88±8.51 (0.16-23.11)	0.89
Chromium	mgkg ⁻¹	0.02±0.03 (0.00-0.12)	0.02±0.02 (0.00-0.08)	0.02±0.02 (0.00-0.05)	0.50
Nickel	mgkg ⁻¹	2.04±2.33 (0.00-5.42)	2.34±2.39 (0.00-5.75)	1.52±1.53 (0.00-3.84)	0.75
Lead	mgkg ⁻¹	4.81±2.53 (1.75-8.89)	4.80±2.43 (1.34-7.11)	3.73±2.27 (0.85-6.92)	0.75

Table 2. Bioaccumulation levels of heavy metals in shrimps of Omodo River in Agbede Wetlands from December, 2012 to May, 2014.

Parameter		Station 1	Station 2	Station 3	FAO limit	p-value
		$\bar{x} \pm SD$ Min-Max	$\bar{x} \pm SD$ Min-Max	$\bar{x} \pm SD$ Min-Max		
Copper	mgkg ⁻¹	6.995 ^{ab} ±0.823 (5.716-8.032)	6.146 ^b ±0.972 (5.021-7.511)	8.130 ^a ±1.074 (6.931-9.524)	30	0.010
Zinc	mgkg ⁻¹	16.530 ±1.020 (15.210-17.614)	16.704 ±1.705 (15.076-19.025)	18.182 ±0.725 (17.055-18.978)	30	0.064
Cadmium	mgkg ⁻¹	0.010 ^a ±0.004 (0.001-0.012)	0.002 ^b ±0.001 (0.001-0.004)	0.006 ^a ±0.003 (0.003-0.012)	0.5	0.003
Vanadium	mgkg ⁻¹	0.001 ±0.001 (0.000-0.001)	0.001 ±0.001 (0.000-0.001)	0.001 ±0.000 (0.001-0.001)		0.162
Chromium	mgkg ⁻¹	0.028 ^a ±0.012 (0.003-0.035)	0.017 ^b ±0.001 (0.016-0.018)	0.017 ^b ±0.003 (0.014-0.021)		0.031
Nickel	mgkg ⁻¹	0.008 ±0.006 (0.001-0.013)	0.003 ±0.002 (0.000-0.005)	0.004 ±0.001 (0.002-0.006)		0.054
Lead	mgkg ⁻¹	0.135 ±0.066 (0.018-0.186)	0.131 ±0.057 (0.017-0.167)	0.198 ±0.023 (0.162-0.219)	0.5	0.073
Cobalt	mgkg ⁻¹	0.043 ^a ±0.006 (0.033-0.049)	0.033 ^b ±0.006 (0.026-0.039)	0.045 ^a ±0.010 (0.032-0.056)		0.029

**Figure 2.** Bioaccumulation Levels in the Whole Body Mass of Shrimps (*Caridina africana* and *C. gabonesis*) from Omodo River (December, 2012 to March, 2014).

In some cases, vanadium concentrations read <0.001 mgkg⁻¹ in the whole body mass of crustaceans. There was no significant difference between the means ($p > 0.05$). Chromium minimum and maximum concentrations ranged from 0.003 mgkg⁻¹ at station 1 to 0.035 mgkg⁻¹ at Station 1 across the seasons. The values were between 0.017 and 0.028 mgkg⁻¹ at stations 2 and 1 respectively. There was a significant difference between ($p < 0.05$) the tested means. Nickel was not detectable at Station 2 in the month of June, 2013 and the values were less than 0.02 mgkg⁻¹ across the stations throughout the wet and dry seasons. The mean concentrations were between 0.003 mgkg⁻¹ at Station 2 and 0.008 mgkg⁻¹ at Station 1. The minimum and maximum values were between below detection limit (BDL) at Station 2 and 0.013 mgkg⁻¹ at Station 1. The mean values were not significantly different from one station to the other ($p \geq 0.05$, $f = 0.054$). Lead temporal and spatial

variations ranged from 0.162 to 0.219 mgkg⁻¹ both at Station 3 across the seasons. Mean concentrations ranged from 0.131 mgkg⁻¹ at Station 2 and 0.198 mgkg⁻¹ at station 3. Meanwhile, Lead concentration was highest 0.219 mgkg⁻¹ at station 3 in December, 2013. Cobalt mean concentrations ranged from 0.033 mgkg⁻¹ at station 2 to 0.045 mgkg⁻¹ at Station 3. The minimum and maximum concentrations of cobalt across the stations were between 0.026 mgkg⁻¹ at Station 2 and 0.056 mgkg⁻¹ at Station 3. There was a significant difference between the tested means ($p < 0.05$, $f = 0.029$).

Discussion

Various studies have been carried out with different tests organisms to examine the levels of bioaccumulation of heavy metals in such organisms within the Niger Delta of Nigeria at large, and elsewhere in the world (Stanek *et al*, 2014). Such studies include; ecological studies and biology of *Callinectes amnicola* in the lower reaches of Warri River (Arimoro and Idoro, 2007), heavy metals concentrations in surface water and bioaccumulation in fish (*Clarias gariepinus*) of Owan River in Edo State by Enuneku *et al* (2013), the determination of heavy metals in crab and prawn in Ojo Rivers, Lagos, Nigeria by Olowu *et al* (2010) and the work by Zabby *et al* (2010) at Bodo Creek, Niger Delta, Nigeria. The other is the investigation by Murugan *et al* (2008) on the bioaccumulation pattern of zinc in freshwater (*Channa punctatus*) after chronic exposure.

Apparently, the concentrations obtained for the bioaccumulation studies of heavy metals using shrimps (*C. africana* and *C. gabonesis*) were generally quite low when compared with the above mentioned literatures. The concentrations of metals were highest with Zn > Cu > Pb

> Co > Cr > Cd > Ni > V. This is contrary to the reports by Enuneku *et al* (2013) for bioaccumulation in fish of River Owan, Edo State, Nigeria, and Enuneku *et al* (2014) for health risk assessment of metals contamination through consumption of *Sesarma angolense* and *Macrobrachium macrobrachium* from Benin River, which harbor more intense human derived impacts compared to water bodies in the Agbede town with reference to Omodo River.

Copper has been reported as an essential element for vertebrates and commonly found in fish tissue (Adeyemo *et al* 2010). In this study the range of values for Cu in shrimps was between 6.146 and 8.130 mgkg⁻¹ which were much lower than the set benchmark of 30 mgkg⁻¹ by FAO (1983). The relatively high concentrations of Cu in the shrimps are a reflection of the background levels of Cu in the sediment. The levels of Zn were relatively high although below the benchmark of 30 mgkg⁻¹ set by FAO (1983). The concentration followed the trend of Zn in the sediments. Accumulation of zinc is known to cause a pathogenic condition like Alzheimer's disease (Murugan *et al* 2008). Besides, increasing concentrations causes increasing mortality in other decapods, such as prawn and crabs (Olowu *et al* (2010). Moore and Ramamoorthy (1984) recorded concentration values of between 4.53 and 5.2 mgkg⁻¹ for shrimps, both in the dry and wet seasons. All other metals (Cd, V, Cr, Ni, Pb and Co) concentration levels were rather very low. A situation contrary to findings on crab and prawn by Olowu *et al* (2010). They all exhibited a trend that closely followed the obtained results in the sediment. It is important to note that the metals had their values within the FAO limits. No seasonal distinction was observed in the concentrations of heavy metals values, rather there was fluctuation across the seasons and stations.

Conclusion

The concentration values obtained for heavy metals in this study have indeed confirmed the non-industrial waste disposal into the water bodies in Agbede Wetlands including Omodo River. The low levels of metal concentrations as recorded in this study, could be attributed to the dominance of the sandy sediment which determines the distribution of cations and nutrients in the environment. Meanwhile, the implication of this study is that the shrimps are safe for consumption by humans and across the trophic levels since the metal concentrations were within FAO limits. This study also suggests that shrimps perhaps, accumulate less metals from the environment due to their feeding habit as both deposit feeders and grazers contrary to deposit feeders.

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