

www.coast.oaustech.edu.ng **COAST JOURNAL OF THE SCHOOL OF SCIENCE** Volume 6, Issue 2. November, 2024 ISSN: 2714-3716

Coast, J. Sch. Sci. 6 (2): 1011- 1020

HEAVY METAL LEVELS IN SEDIMENT AND C*allinectes sapidus* **OF OKERENKOKO WATERFRONT, DELTA STATE, NIGERIA**

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https://doi.org/10.61281/coastjss.v6i2.1

Abstract

Efuent deposition increases sediment pollution. Information on heavy metal (HM) levels of Okerenkoko Waterfront (OWF) are limited. This study investigated the present levels of HM in OWF and their impacts on *Callinectes sapidus*. Spatially, OWF was stratied into three stations (1, 2 and 3) based on proximity to key industrial activities, while monthly stratification covered

April to July, 2023. Sediment and *C. sapidus* samples were collected monthly, air-dried at room temperature and preserved in Bouin's fluid respectively. Samples were digested and concentrations of HM (Iron and Copper) mg/Kg determined using Atomic Absorption Spectrophotometer. Data obtained were analyzed using descriptive statistics and ANOVA at $a_{0.05}$. Spatially, significantly highest (11.64 ± 0.11; 3.41 \pm 0.32) and least (4.99 \pm 2.03; 3.26 \pm 0.72) levels of iron and copper recorded in sediments occurred in 1 and 3, while it ranged from 5.02 ± 3.03 to 13.18 ± 0.11 and 7.10 ± 1.46 to 18.19 ± 0.38 for copper and iron in May and July respectively. Spatially, highest (8.49 ± 1.64) and least (4.57 ± 1.17) levels of iron in the stomach of *C. sapidus* occurred in 3 and 1, while it ranged from 10.13 ± 4.19 to 14.94 ± 2.33 in June and July. Copper concentration ranged from 1.12 ± 0.01 to 5.15 ± 2.09 in May and July in the stomach of *C. sapidus*. Concentrations of HM recorded exceed recommended limits. Survival of *C. sapidus* in OWF has been threatened. Results obtained could serve as baseline reference.

Key words: Benthic sediment, Atlantic blue crab, Heavy metals, Anthropogenic effluents, Pollution

Sediment serves as both habitat and source of food for certain crustaceans species (Ediagbonya *et al.,* 2016; George and Abowei, 2018). Crab burrow into the sediment for protection and to find preys (Ediagbonya *et al.,* 2014). Too much sedimentation can smother benthic

Introduction organisms such as *Callinectes sapidus* (*Decapoda*: *Portunidae*; Rathbun, 1896) and their burrows, making it extremely frustrating for them to find food, hindering escape from predators and disrupting their life cycles (Ewutanure *et al.,* 2022). Alteration in sediment due to anthropogenic activities such as dredging or coastal development have

been reported to destroy essential breeding and nursery areas of crustaceans (Al-Shami *et al.,* 2011; Ediagbonya and Adesokan, 2019) because of the expression atmospheric deposition which is wet and dry deposition (Ediagbonya *et al.*, 2016).

Sediments accumulate and store pollutants over time (Asibor, 2016; Ediagbonya and Adesokan, 2019). Industrial effluents, runoff from agricultural and urban activities and atmospheric deposition introduce pollutants (heavy metals, hydrocarbon and pesticides) into surface water (Seiyaboh *et al.* 2013; 2016; Ajayi, 2018). Heavy metals are adsorbed by sediment particles and persists thereby impacting sediment quality (Hadjiliadis, 2012; Asibor, 2016). Pollutants presence in sediments constitutes harm to benthic organisms (worms, insects, crustaceans, and mollusks) because they bio-accumulate in the tissues of benthic organisms thereby causing impaired growth, decrease in reproductive rates, physical deformities and mortality (Uncumusaoglu *et al.,* 2016; Akankali and Davies, 2018). Benthic organisms (in-fauna and epi-fauna) ingest contaminants directly during feeding (Ayotunde *et al.,* 2012).

Sediments act as a source of pollution to surface water column, while suspended sediments transported along water column affect filter-feeding organisms and fish gills (Ediagbonya and Adesokan, 2019). Suspended sediments transport attached pollutants thereby affecting water quality and negatively impacting the aquatic food chain (Boohene and Agbasah, 2020). Sediments pollutants have the ability to persist with long-term effects on aquatic biota and they can serve as a continual source of pollution, releasing the pollutants slowly over time and sustaining the pollution levels in the water column (Asare *et al.,* 2018).

The *C. sapidus* is native to the waters of the

Gulf of Guinea and has a life span of about three years and can grow up to a width of 23 cm. They have three pairs of walking legs, while their rear legs that are paddle-like are used for swimming. *C. sapidus* are omnivores and use their powerful claws to gather food (Rady *et al.,* 2018).

Males and females are easily distinguished by their abdominal shape (known as the apron) and by colour differences in the chelipids (claws). The abdomen is long and slender in males, but wide and rounded in matured females, while an immature female has a triangular shaped abdomen. The claws are orange coloured with purple tips in females, while it is blue with red tips in males. Females mate during their final molt and the males will carry the females around to protect them from predators.

The females of *C. sapidus* can produce between 689,356 and 3,438,122 with an average of 2,006,974 eggs per brood (Severino-Rodrigues *et al.,* 2013). They also store sperm from their mating encounter and spawn multiple times, while the eggs are carried under the abdomen until they hatch into larvae (Hines *et al.,* 2003). Females carrying egg masses are called sponge crabs. The eggs of *C. sapidus* hatch in saline waters of inlets, coastal waters and mouths of rivers are carried to the ocean by ebb tides (Wikipedia, 2023). The survival of benthic fauna species in surface waters depends on the sediment quality. Effluent deposition increases heavy metal concentrations in sediment. Information on heavy metal levels and their impacts on benthic fauna species of Okerenkoko Waterfront (OWF) are limited. Hence, this study was carried out to investigate the present levels of heavy metal concentrations in sediment of OWF and their impacts on *C. sapidus*.

Materials and Methods

Study Area

Okerenkoko Waterfront (OWF) is located on

latitudes 5°37'62"N and 5°37'16" N of the equator and longitudes 5°23'69" E and 5°2'12" E of the Greenwich meridian (Figure 1). The geology of the region consists of an alluvial sedimentary basin and basement complex with a relatively flat landscape. The OWF is an estuary ecosystem that serves as habitat for aquatic organisms such as *C.*

sapidus and also as a source of livelihood for the communities in the area. The estuary is surrounded by creeks and various red and white mangroves. The primary occupation of the people living in the Okerenkoko Estuary is subsistence fishing (Ewutanure and Binyotubo, 2021).

Figure 1: Map of study area. (Source: Adopted from Ewutanure and Asogwa, (2023).

Sampling Techniques

The OWF was spatially stratified into three stations (1, 2 and 3) based on closeness to key anthropogenic effluents. Two sampling areas per stations were randomly selected, while temporal stratification covered April -July, 2023. The exact locations of all sampling stations were determined using Garmin GPSMAP eTrex 10 type sensors. Sediments and *C. sapidus* samples were collected on monthly basis by using a lift net.

Sediment samples were collected from the inter-tidal zone by using a hand trowel and immediately transferred into an aluminum foil and placed in ice chest containers for onward transportation to the laboratory where they were air-dried at room temperature and kept for heavy metal analysis (AOAC, 1990). The *C. sapidus* samples were collected with the aid of the circular lift net and identified to species level using standard key (Schneider, 1990), while their stomach contents were harvested and preserved in a Bouin's fluid as described by FAO/SIDA, (1983) for heavy metal analyses.

Analytical Techniques

Sediment samples digestion and heavy metals determination: About 1.00g of airdried sediment sample was ground in a mortar and heated to reddish brown in a furnance and moistened using de-ionised water. About 1 mL of 60% perchloric acid and 20 mL of 40% hydrofluoric acid were added. The content was heated to dryness on a sand bath at 180°C. It was allowed to cool, while about 15 mL of 10% hydrochloric acid was added. The mixture was heated in a crucible to dryness (Baird *et al.* 2017), while heavy metal concentrations in the sediment were determined using Atomic Absorption Spectrophotometer (AAS).

Digestion of *C. sapidus* for heavy metal determination: Following the methods described by AOAC (1990), 5.00 g of *C.*

sapidus was oven-dried at 105°C in a Gallenkamp oven to a constant weight. The sample was then ground into powdery form with the aid of a pestle and mortar. The powdered samples were further dried to constant weights, while 0.50g was collected for digestion with the aid of an electronic sensitive weighing balance and placed in a 50 mL conical flask where 20 mL of $HNO₃$, 2 mL of $H₂SO₄$ and 4 mL of perchloric acid (a catalyst) were added (AOAC, 1990). Thereafter, the sample was transferred onto a hot plate in a fume cupboard and heated for one hour at a temperature of 200 $\mathrm{^o}\mathrm{C}$ which was later reduced to 70° C, and digestion allowed to continue. Samples with black fumes were further acidified with 10 mL of $HNO₃$ and the digestion was allowed to continue until the white fumes of per chloric acid disappeared leaving a clear yellowish solution. The resultant yellowish solutions were allowed to cool and then filtered. The filtrate was placed in the standard volumetric flask and made up to 50 mL mark with distilled water (Baird *et al.,* 2017). Thereafter, heavy metals in *C. sapidus* samples were measured by using AAS (ASTM, 2006).

Data Analysis

Data obtained from the study were analysed descriptively for their central tendencies. Significant differences were established using one-way analysis of variance (ANOVA) at p˂0.05. Results were presented according to their monthly and spatial mean variances. All analyses were done using the Statistical Package for the Social Sciences (SPSS Version 20.0).

Results

Concentrations of heavy metals in sediment samples of Okerenkoko waterfront among stations and months are shown in Tables 1 and 2, respectively. The concentrations of Fe ranged from 4.99±2.03 (mg/Kg) to 11.64±0.11 (mg/Kg) in stations 3 and 1; Cu (1.99±0.01, 3.41±0.32) (mg/Kg) occurred in stations 2

and 1; Ni (3.01±0.15, 5.32±0.01) (mg/Kg) occurred in stations 2 and 1, respectively. The concentration of Zn and Al were below

detectable limits. Significant differences existed among the concentrations of heavy metals recorded in sediment samples.

Note: BDL = Below detectable limit, a-c Means with different letter superscripts along a row are significantly different (p<0.05).

The highest (17.72 ± 0.34) mg/Kg and least (13.18 ± 0.11) mg/Kg concentrations of Fe were recorded in April and May, Cu ranged from 5.02 ± 3.03 (mg/Kg) to 7.10 ± 1.46 (mg/Kg) in May and July, while Ni ranged from 3.97 ± 0.67 to 5.96 ± 1.19 (mg/Kg) occurred in May and July, respectively, while Al was below detectable limits. Significant differences existed among the concentrations of Fe recorded in sediment samples.

Table 2: Monthly distribution of heavy metals in sediment of Okerenkoko waterfront, Niger Delta, Nigeria between April to July, 2023.

Metals		FEPA,			
	April	May	June	July	(1991)
Fe (mg/Kg)	17.72 ± 0.34	13.18 ± 0.14	15.14 ± 2.93	18.19 ± 0.38	< 0.300
Cu (mg/Kg)	6.76 ± 1.33	5.02 ± 3.03	6.90 ± 0.24	7.10 ± 1.46	0.026
Zn (mg/Kg)	BDL	BDL	BDL	BDL	0.004
Ni (mg/Kg)	5.19 ± 4.17	3.97 ± 0.67	4.49 ± 2.19	5.96 ± 1.91	0.015
Al (mg/Kg)	BDL	BDL	BDL	BDL	0.052

Note: BDL = Below detectable limit, a-d Means with different letter superscripts along a row are significantly different (p<0.05).

Concentrations of heavy metals in *C. sapidus* samples of Okerenkoko waterfront among stations and months are shown in Tables 3 and 4, respectively.

The concentrations of Fe in *C. sapidus* stomach ranged from 4.57±1.17 (mg/Kg) to 8.49 ± 1.64 (mg/Kg) in stations 1 and 3; Cu (4.71±0.91, 5.96±1.03) mg/Kg occurred in stations 3 and 2; Ni (1.26±0.13, 3.89±0.51) mg/Kg occurred in stations 2 and 1, respectively, while Zn and Al were below detectable limits. Significant differences existed among the concentrations of heavy metals recorded in the stomach of *C. sapidus* samples.

Metals		FEPA, (1991)		
		◠	З	
Fe (mg/Kg)	$4.57 \pm 1.17^{\rm a}$	6.54 ± 0.12^b	8.49 ± 1.64 ^c	0.001
Cu (mg/Kg)	5.09 ± 2.31 ^a	5.96 ± 1.03 ^a	4.71 ± 0.91 ^a	0.009
Zn (mg/Kg)	BDL	BDL	BDL	0.003
Ni (mg/Kg)	$3.89 \pm 0.51^{\circ}$	1.26 ± 0.13^a	$2.94 \pm 0.35^{\rm b}$	0.004
Al (mg/Kg)	BDL	BDL	BDL	0.007

Table 3: Spatial distribution of heavy metals in *C. sapidus* **stomach of Okerenkoko waterfront, Niger Delta, Nigeria between April to July, 2023.**

Note: BDL = Below detectable limit, a-c Means with different letter superscripts along a row are significantly different (p<0.05).

The highest (14.94 \pm 2.33) mg/Kg and least (10.13 ± 4.19) mg/Kg concentrations of Fe were recorded in July and June, Cu ranged from 1.12 ± 0.01 (mg/Kg) to 5.15 ± 2.09 (mg/Kg) in May and July, while Ni ranged from 3.97 ± 0.67 to 5.96 ± 1.19 (mg/Kg) occurred in May and July, while Ni (1.11±0.12, 3.97±0.02) Kg occurred in April and July, respectively. But Zn and Al were below detectable limits. Significant differences existed among the concentrations of Fe and Ni recorded in the stomach of *C. sapidus* samples.

Table 4: Monthly distribution of heavy metals in *C. sapidus* **stomach of Okerenkoko waterfront, Niger Delta, Nigeria between April to July, 2023.**

Metals		FEPA, (1991)			
	April	May	June	July	
Fe (mg/Kg)	11.45 ± 1.97 ^b	$13.19 \pm 2.06^{\circ}$	10.13 ± 4.19^a	14.94 ± 2.33 ^d	0.001
Cu	4.05 ± 1.01 ^b	$1.12 \pm 0.01^{\text{a}}$	4.14 ± 1.22	5.15 ± 2.09 ^b	0.009
(mg/Kg)					
Zn (mg/Kg)	BDL	BDL	BDL	BDL	0.003
Ni (mg/Kg)	1.11 ± 0.12^a	3.17 ± 1.91 ^c	2.45 ± 0.61 ^b	3.97 ± 0.02 c	0.004
Al (mg/Kg)	BDL	BDL	BDL	BDL	0.007

Note: BDL = Below detectable limit, a-d Means with different letter superscripts along a row are significantly different (p<0.05).

Discussion

Concentrations of Fe, Cu and Ni recorded during the study exceeded the acceptable limits of 0.300, 0.026 and 0.015 in sediment and 0.001, 0.009, 0.004 in crab respectively (FEPA, 1991). This result agrees with Aghoghovwia *et al.,* (2015); Ediagbonya *et al*., (2016) that reported increased anthropogenic activities and discharge of untreated effluents as the cause of elevated metal levels in water and sediment of Warri

River, Niger Delta, Nigeria. Increase heavy metal concentration than the acceptable standard is associated with severe damages to the gills of fishes (Ediagbonya and Adesokan, 2019; Adegbola *et al.,* 2021).

Some impacts of heavy metals pollution on fish include inflammatory cells within the hepatic tissue, inflammation of gill lamellae, disruption of hepatocytes, atrophy of lamellae, cellular breakdown of gills, clogging of gills with mucus, necrosis of hepatocytes,

retardation in growth and maturation (Olaifa *et al.*, 2004). The flora and fauna species can take up heavy metals bound in sediment matrix during feeding and nutrients adsorption, while excessive levels of heavy metals could be injurious to benthic fauna species (Izah *et al.,* 2015). Higher levels of Fe, Cu and Ni may lead to the extinction of pollution sensitive aquatic organisms (Ewutanure and Olaifa, 2018).

Ewutanure *et al.,* (2022) reported that higher levels of heavy metals in the aquatic environment could disrupt ecosystem balance, leading to its impaired functions, reduced biodiversity and decline of pollution sensitive crustaceans. Additionally, heavy metals can bio-accumulate in the aquatic food chain and negatively impact higher level predators, including humans (FAO, 199I; Yujun *et al.,* 2008; Ajayi, 2018). They contaminate surface water and sediment for a long time thereby making the sediment unsuitable for benthic invertebrate species (Asare *et al.* 2018). Heavy metals interfere with natural processes (nutrient cycling, photosynthesis and respiration) in surface waters. This disruption can lead to reduced productivity (Adebowale *et al.,* 2008; Ayandirana *et al.,* 2018).

Though, the concentrations of Al and Zn recorded within months were below detectable limits, tt is worthy of note that specific impacts of Fe, Cu and Ni exposure on the hepatopancreas of *C. sapidus* and other crustaceans may vary depending on the species and the level and period of exposure. Heavy metals (Fe, Cu and Ni) can have significant impacts on water quality and threaten the survival of fauna larvae and human health (Ayeni *et al.,* 2011; Iloba and Ruejoma, 2014).

Conclusion

The concentrations of heavy metals (Fe, Cu and Ni) in water, sediment and *C. sapidus* obtained from OWF exceeded recommended standards (FEPA, 1991). Results of this study showed that *C. sapidus* in OWF bioaccumulated Fe, Cu and Ni. Hyperplasia observed in the gill of *C. sapidus* may be associated with its contact with pollutants and this can lead to insufficient utilization of DO concentration in water. It has been reported that hyperplasia gills can cause mass mortalities of *C. sapidus* fry in surface water. Data obtained from this study will serve as a baseline for further studies. Regular monitoring of sediment quality of OWF should be encouraged so as to ensure the sustainable management of its fish stock.

Acknowledgements

The authors are grateful to the Management of the Multidisciplanary Laboratory, University of Ibadan, Ibadan, Nigeria for granting us access to the Laboratory for the analyses of the collected samples used for this study. My gratitude also goes to Mrs. Victoria Kevwe EWUTANURE of the Post Primary Education Board, Delta State, Nigeria for her financial support and encouragement throughout the period of this study.

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