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Assessment of Water, Sediment and Crab (Callinectesamnicola) Contamination by Heavy Metals in Ijala Creek, Ekpan, Delta State, Nigeria

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Abstract: *Heavy metals such as; Nickel (Ni), Lead (Pb), Chromium (Cr), Iron (Fe), Cadmium (Cd), Manganese (Mn), Zinc (Zn), Copper (Cu) and Vanadium (V) were assessed in water, sediment and crab (Callinectesamnicola) from three stations along Ijala creek. The creeks receive effluents discharges from industrial activities and few human settlements within the area.Samples of water, sediments and crab (Callinectesamnicola) were processed and analysed for heavy metals using various analytical techniques. The results showed thatthe heavy metal contaminationin sediments is more than that of the crabs andthe crabs accumulate these metals more than the water. Cadmium had the highest Biological Concentration Factor (BCF) when compared with the Biological Concentration Factors of other metals. Atomic Absorption Spectrophotometer was used in the determination ofthe selected heavy metals. The concentration of heavy metals obtained were in the orders: water had Fe> Zn>Mn> Cu> Ni> Cd> Cr>Pd> V; sediment had Fe> Zn> Cu> Ni> Cd>Mn>Pb> V and crab had Fe> Cd> Cr> Zn> Cu>Mn> Ni>Pb> V.The concentration of metals in water,sediment and crab showeda significant difference ($P < 0.05$). Fe had the highest concentrated among the heavy metals in the three sample matrix (water, sediment and crab) and its value exceeded the background value and also above the target and intervention values for sediment micro-pollutant standard. The contamination ofIjala creek by heavy metals increased in this order; station III> station II > station I. The study observed fluctuation in heavy metal concentration in the creek and suggested stringent environmental monitoring of the creek.*

Key Word: *Pollution, Heavy metal, Ijala creek, Water, Sediment and Crab, Contamination.*

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I. Introduction

One of the most affected phases in environmental pollution is the ecosystem, especially the surface water. This is because the pollutants in air and land end up in the aquatic system by means of local precipitation, leaching or water runoff (Issa et al., 2011).

Heavy metals in recent times havefoundtheir way in to the ecosystem due to high increase in industrial activities. Also, significant amounts of agricultural and municipal wastes are discharged into the environment. Pollutants of these natures enter atmospheric and hydrological circulation and finally end on the river beds, back swamps, and in the marine environment where both lacustrine and marine sediments are continuously enriched with all kinds of contaminants (Ako and Salihu, 2004).

The major causes of surface water pollution have been attributed to sewage, industrial wastes and agricultural chemicals such as fertilizers and pesticides (Yim et al., 1999).On several occasions,unwanted elements have been found in mineral fertilizers such as cadmium (Cd) and chromium (Cr). These trace metals are much more likely available to biota than those in soils (Singh et al., 1997).

Davies et al., (2006) reported that contaminants such as trace metals, phosphorous and polycyclic aromatic hydrocarbons are consumed and concentrated by sediments in the aquatic system.

One of the challenges in developing nations including Nigeria is increase in pollution load as a result of highinflow of effluents of different kinds from human activities, which have become a threatto the quality of water (Nduka and Orisakwe, 2009). Human activities stress aquatic systems and affect biota at different levels and temporary scales.

The contamination of sediments by heavy metals in small concentrations could have serious resultant effectson the environment since itserves as reservoir for pollutants and also as potential source of pollutants to the water column, organisms, and ultimately human beings that consume these organisms. Alethal and sub-lethal effect in benthic and other sediments associated organisms in contaminated sedimentshas been reported by United States Environmental Protection Agency (2001). The severity of sediment contamination in UnitedSates has been documented in the National Sediment Inventory (NSI) which shows thousands of data on the affected areas throughout the country.

Nigeria's largest Petroleum refinery is the Warri Refinery and Petrochemical Company Limited which has the capacity of refining one hundred and twenty-five thousand (125,000) barrels of crude oil per day.Heavy metals are found in different proportions in Nigerian crude oil (Nduka and Orisakwe, 2009). The Warri Refinery and Petrochemical Company (WRPC) increases the problems by discharging its untreated effluents in to the adjoining surface waters. Therefore this study is important since it will acertain the level of contamination by heavy metals in Ijala creek.

This work covers the sampling of whole sediment, water and crabs holding time, sample manipulation and the level of contamination of heavy metals in Ijala creek.

II. Materials And Methods

Study Area

Ijala creek lies between latitude 5º.10´-6º.20´N and longitude 6º.10-6º.21´E. It is found in Uvwie local government area of Delta state, Nigeria and flow from low population density of Ijala, Ifie-kporo and Aja-etan communities to the Tori creek (Figure 1). The annual rainfall of the area is about 3,000mm with tropical humidity of semi-hot equatorial type (Alakpodia, 2001). The wet season is observed from April to October but occasional precipitationoccurs in the dry season observed in November to March. The relative humidity of the area is high and increases from 70% in January to 80% in July. The average atmospheric temperature of the area is about 25.5°C in the rainy season and about 30°C in dry season (Chukwujindu et al., 2007).

The creek is located within mangrove swamp of equatorial rain forest of South – Southern Nigeria and surrounded by several communities and industries like Warri Refinery and Petrochemical Company Limited, Chevron Nigeria Limited and Matix Energy Services Limited among others. Both municipal and industrial wastes from these communities and industries are discharged into the water body of this creek. The stream also receives heavy load of pollution discharges from other activities resulting from Mechanic Workshop, River Port, Fishing and Timber logging.

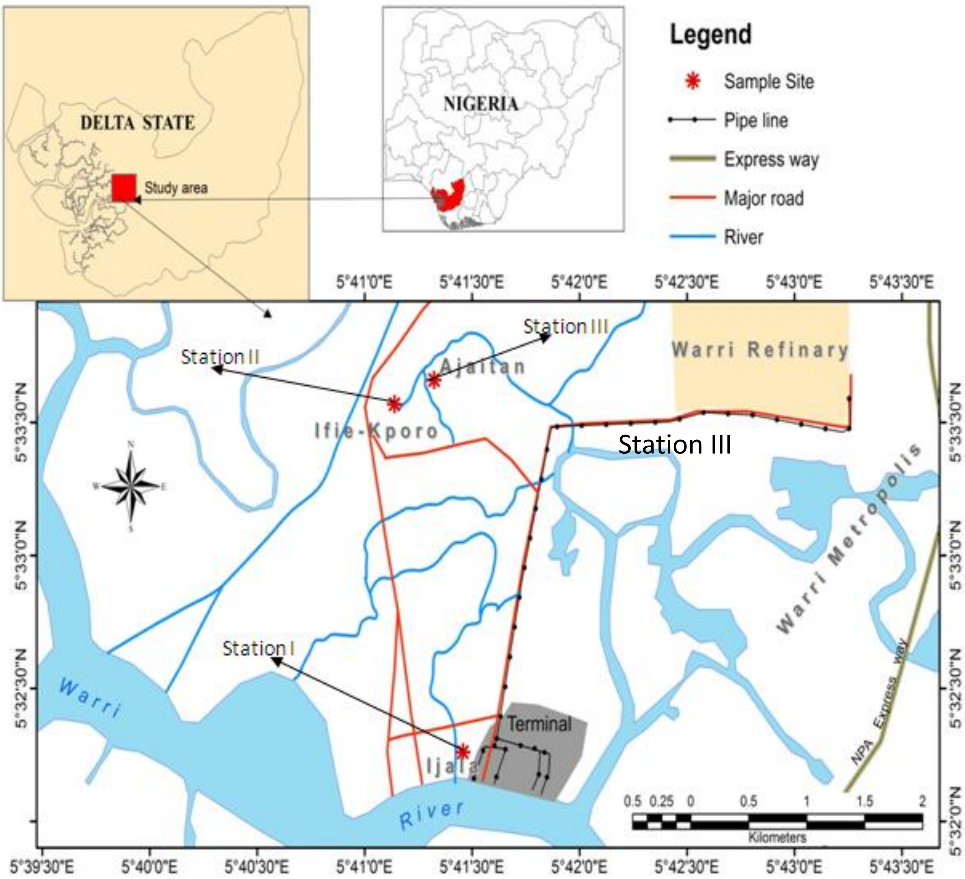

Fig. 1: Map of the study area showing the sampling stations

Sampling and Sample preparation

A. Water

A decontaminated Kemmerer bottle device was used in collecting water samples according to (APHA, 2005) from the three designated locations along Ijala creek.

B. Sediment

Sediment samples were collected using Birge-Eckman grab sampler and samples collected were air dried for two weeks before grounded in to fine particles in a mortal and sieved through a 2mm sieve. An extraction procedure was adopted fromBinning and Baird,(2001), using $HClO_4$ and HNO_3 at a 2:1 ratio (v/v),followed by addition of concentrated HNO_3 (20m1) and filtered in to 50ml volumetric flask through Whatman 42 filter paper. The volume was made up to 50m1 mark with distilled water.

C. Crab

A square lift net trap was used to collect the crab samples and the debris were removed by rinsing thoroughly with distilled water. They were then drained in filter, weighed, wrapped in aluminium foil and then frozen prior to analysis (Olowu et al., 2010). The extraction techniques was adapted from Canli and Atli,(2003) by weighing the dried samples at intervals of 4 hours until a constant weight was obtained and grounded to fine particles. Grounded samples weresieved with a 0.02 mm sieve.0.5 g each of the samples were weighedinto clean dried beakers, 100 ml and5 ml of aqua regiaHCl and HNO_3 (3:1) were then added to the sample for digestion. Each of the digested samples were filtered into a graduating cylinder and the volumemade up to50 ml mark with distilled water.

ANALYSIS OF THE HEAVY METALS

The Atomic Absorption Spectrophotometer (PG 2900) was used in determiningthe concentration of heavy metals in various samples.

III. Results

The concentrations of heavy metal in water, sediments and crabs are presented in tables 1, 2 and 3

Table 1 shows the mean concentrations, standard deviation, minimum and maximum values of the selected heavy metals in the water samples.

Table1: Heavy metal concentrations in water samples.

	Ijala Community (station I)	**Efie- Kporo Community (station II)**	**Aja- Etan Community (station III)**		
Parameters	$\bar{x}$±SD (Min-Max)	$\bar{x}$±SD (Min-Max)	$\bar{x}$±SD (Min-Max)	P-Value	Standard(WHO,2004)
pH	6.153±0.181 (5.790-6.350)	6.236±0.085 (6.130-6.430)	6.244±0.142 (5.930-6.460)	P>0.05	6.5-8.5
Nickel (mg/l)	0.018±0.008 (0.010-0.030)	0.022±0.018 (0.001-0.050)	0.031±0.007 (0.020-0.050)	P>0.05	0.02
Lead (mg/l)	0.001±0.000 (0.000-0.001)	0.001±0.000 (0.001-0.001)	0.002±0.003 (0.001-0.010)	P>0.05	0.01
Chromium (mg/l)	0.005±0.000 (0.005-0.005)	0.005±0.000 (0.005-0.005)	0.005±0.000 (0.005-0.005)	P>0.05	0.05
Iron (mg/l)	1.090±0.119 (0.870-1.280)	1.130±0.169 (0.970-1.470)	1.096±0.114 (0.960-1.320)	P>0.05	0.3
Cadmium (mg/l)	0.005±0.000 (0.005-0.005)	0.005±0.000 (0.005-0.005)	0.005±0.000 (0.005-0.005)	P>0.05	NG
Manganese (mg/l)	0.011±0.011 (0.005-0.040)	0.017±0.017 (0.005-0.050)	0.011±0.007 (0.005-0.030)	P>0.05	0.05
Zinc (mg/l)	0.144±0.049 (0.090-0.240)	0.168±0.035 (0.100-0.22)	0.207±0.058 (0.130-0.280)	P>0.05	5
Copper (mg/l)	0.031±0.024 (0.010-0.080)	0.032±0.017 (0.010-0.060)	0.040±0.021 (0.020-0.080)	P>0.05	1.0
Vanadium (mg/l)	0.001±0.000 (0.001-0.001)	0.001±0.000 (0.001-0.001)	0.001±0.000 (0.001-0.001)	P>0.05	NG

P>0.05 – No significant difference

P<0.05 – Significant difference

NG – not mentioned in WHO guideline

Similar superscript row wise – No significant difference

Table 2 shows the mean concentrations, standard deviation, minimum and maximum values of the selected heavy metals in the sediment samples.

Table 2: Heavy metal concentrations in sediment samples.

	Ijala Community (station I)	**Ifie-kporo Community (station II)**	**Aja- Etan Community (station III)**		
Parameters	$\bar{x}$±SD (Min-Max)	$\bar{x}$±SD (Min-Max)	$\bar{x}$±SD (Min-Max)	P-Value	
pH	6.266±0.178 (5.950-6.520)	6.042±0.250 (5.410-6.260)	6.263±0.324 (5.850-6.770)	P>0.05	
Nickel (mg/l)	21.07±6.48 ^{B} (11.27-28.80)	22.41±12.18 ^{B} (9.45-40.19)	30.79±2.12 ^{A} (28.64-34.60)	P<0.05	
Lead (mg/l)	1.84±1.19 (0.36-3.04)	1.29±0.78 (0.54-3.10)	2.06±0.95 (0.76-3.07)	P>0.05	
Chromium (mg/l)	0.48±0.12 ^{B} (0.29-0.66)	0.56±0.14 ^{A} (0.42-0.85)	0.64±0.07 ^{A} (0.52-0.79)	P<0.05	
Iron (mg/l)	778.20±169.53 (629.00-1002.00)	790.20±115.90 (602.00-1008.00)	731.20±173.14 (478.00-1008.00)	P>0.05	
Cadmium (mg/l)	17.48±3.85 ^{C} (12.41-25.32)	22.56±4.88 ^{B} (11.20-28.60)	28.87±4.22 ^{A} (21.70-33.80)	P<0.05	
Manganese (mg/l)	16.81±9.36 (10.40-42.60)	21.63±15.27 (9.86-50.80)	20.82±5.85 (14.76-32.60)	P>0.05	
Zinc (mg/l)	86.77±48.43 (21.40-134.00)	81.10±50.46 (12.40-134.00)	97.12±31.59 (51.80-149.00)	P>0.05	
Copper (mg/l)	21.95±6.14 ^{B} (10.86-28.45)	26.21±9.88 ^{B} (14.25-40.19)	44.55±15.54 ^{A} (26.07-64.26)	P<0.05	
Vanadium (mg/l)	0.06±0.03 ^{A} (0.01-0.11)	0.01±0.00 ^{B} (0.01-0.01)	0.06±0.02 ^{B} (0.01-0.07)	P<0.05	

P>0.05 – No significant difference

P<0.05 – Significant difference

Similar superscript row wise – No significant difference

Table 3 shows the mean concentrations, standard deviation, minimum and maximum values of the selected heavy metals in crab samples

Table 3: Bioaccumulation of heavy metals in the Crab *(Callinectesamnicola)*.

	IjalaCommunity (Station I)	**Efie- Kporo Community (station II)**	**Aja- Etan Community (station III)**		
Parameters	$\bar{x}$±SD (Min-Max)	$\bar{x}$±SD (Min-Max)	$\bar{x}$±SD (Min-Max)	P-Value	
Nickel (mg/l)	0.155±0.082 (0.080-0.340)	0.208±0.201 (0.070-0.670)	0.295±0.108 (0.180-0.519)	P>0.05	
Lead (mg/l)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.019±0.028 (0.010-0.100)	P>0.05	
Chromium (mg/l)	0.050±0.000 (0.050-0.050)	0.155±0.212 (0.050-0.660)	0.050±0.000 (0.050-0.050)	P>0.05	
Iron (mg/l)	9.025±6.719 (3.660-21.600)	5.511±3.534 (2.840-12.400)	6.514±1.828 (4.680-9.160)	P>0.05	
Cadmium (mg/l)	2.629±2.025 (0.770-6.060)	1.448±0.608 (0.630-2.330)	2.152±1.317 (0.970-4.850)	P>0.05	
Manganese (mg/l)	0.050±0.000 (0.050-0.050)	0.050±0.000 (0.050-0.050)	0.050±0.000 (0.050-0.050)	P>0.05	
Zinc (mg/l)	0.045±0.021 ^{B} (0.030-0.090)	0.068±0.034 ^{B} (0.010-0.120)	0.105±0.055 ^{A} (0.030-0.210)	P<0.05	
Copper (mg/l)	0.100±0.037 ^{B} (0.050-0.160)	0.084±0.044 ^{B} (0.020-0.140)	0.215±0.067 ^{A} (0.110-0.320)	P<0.05	
Vanadium (mg/l)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	P>0.05	

P>0.05 – No significant difference

P<0.05 – Significant difference

Similar superscript row wise – No significant difference

IV. Discussion

Among the metals analyzed, Iron (Fe) recorded the highest concentration of 1.10mg/l, Lead (Pb) and Vanadium (V) had observed with concentration level of 0.001mg/l. The low concentration of heavy metals observed in water agreed with the finding of Topouogluet al.,(2002) who previously worked on samples from the creek. The concentration of heavy metals in water at station II was observed to be higher when compared with other sampling stations; this could be attributed to waste from Warri Refinery and human settlement around the creek.The high concentrations of Iron (Fe)observed, also agreed with the reports of Albert, et al.,(2010), Abolude et al., (2009) andAkanet al,(2011).

Analysed metals showed no significant difference in all the sampling stations. The measured values of heavy metals, however, are within safe limits for drinking water (WHO, 2003) with exception of Iron (Fe) which was above the limit. The relative dominance of the heavy metals in water was observed in this sequence: Fe>Zn>Mn>Cu>Ni>Cd>Cr>Pd>V.

The colour of the sediments which varied from brown to reddish brown across the sampling stations could be due to the various concentrations levels of iron content.However, the overall assessment of sediment contamination is difficult since the concentration of heavy metals varies from onelocation to another.

It was also observed that the sediments accumulated more of these metals than water and crab sampleswhich agreed with what was reported byEjaet al.,(2003). Sediment holds more than 99 percent of metal deposits in aquatic system (Magalhaes et al., 2007).

The observed high concentrations of Fe in sediments have no identifiable point source discharge rather than lithological or crustal origin (Davies et al., 2006). There is no doubt that wastes generated due to human activities are discharged on land or streams. In and around the study area, the wastes were transported by surface run-off to the water body by rain. Thus, contribution from run-off in this regard may be significant as evident in the concentration distribution of these metals in Ijala creek sediment (Table 2).The concentration of Fe, Zn and Cu in sediments exceeded background values (Nasr et al 2006, Brciela-Alonso et al., 2003) and were also above the DPR (2002) range of target and intervention values for micro-pollutant sediment. The concentration of heavy metals in sediment were of the order; Fe > Zn > Cu > Ni > Cd >Mn>Pb> V.

Manganese (Mn) concentration in sediment wasbelow the background value of 790mgkg^{-1} (18, 19). This concentration therefore, poses no threat to the environment but need to be monitored to avoid further increase.

Lead (Pb), Manganese (Mn), Iron (Fe) and Zinc (Zn) shows no significant difference within locations. The correlation coefficient between the metal levels in water, sediment for the ten (10) month variation show high significance ($p<0.05$) to direct correlation between some of the metals. The high correlation between metals indicates common lithological or crustal sources for the metals rather than the anthropogenic sources (Akan et al., 2010).

The highest mean concentration level of 7.016mgkg^{-1} was observed in Chromium while vanadium was found to have lowest mean concentration level of 0.001mgkg^{-1}.

Cadmium had a mean value of 2.08 mgkg^{-1}which was considered to be high, which could be attributed to the activities of Warri Refinery and loading terminal located in the area though it shows no significant difference ($P>0.05$).

Low concentration of Zn, Cu, Co, Mn, and Hg was observed since crustaceans excrete themin the urine (13). The concentrations of heavy metals in crab were in the following order; Fe > Cd > Cr > Zn > Cu >Mn> Ni >Pb> V.

Metals analyzed show no significance difference with the exception of Zn and Cu that showed a great difference within the sampled stations.

The biological concentration factor (BCF) was observed to behigh when compared to the order of uptake of metals and the study shows that crabs have high potential to accumulate these metals. The BCFof heavy metals in this study followed theorder;

Cd > Cr >Pb> V > Ni > Fe >Mn> Cu > Zn.

The correlation between the metal levels in the sediment and bioaccumulation of various heavy metals in crab at the studied stations show high significance ($p<0.05$).

Therefore, it can be deduced that cadmium content in Ijala creek poses a risk to the ecosystem and the source(s) of this pollutant need to be monitored.

V. Conclusion

This study revealedthat the concentrations of heavy metals like Pb, Cr, Mn, Ni, Zn, Cu, V and Cd in the water, sediment and crab samples are low and require monitoring to prevent any further increase. The concentration ofFe is higher when compared to the WHO reference level, background value and target and intervention values for micro pollutant for standard sediment which may constitute risk to the environment. The concentration of heavy metals in Ijala creek increases in this order; station III > station II > station I. Higher concentrations of heavy metals observed in station III may be due to discharge of industrial and municipal wastes, geology of river bed and catchment area.

However, stringent environmental monitoring of this creek is required to check it contamination by heavy metals.

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