Assessment of Human Health Risk from Heavy Metal Loads in Freshwater Clam, Ergeria radiata, from the Nun River, Niger Delta, Nigeria

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Abstract

The Nun River where the present study took place is one of the two arms of River Niger system traversing Bayelsa State, Nigeria before emptying into the Atlantic Ocean. It is home to a number of commercial fish and shellfish species, some of which are endemic, including the highly relished freshwater clam (*Ergeria radiata*) in the Niger Delta region of Nigeria. The Nun River is subjected to a myriad of human induced contaminations from oil and gas activities, agricultural runoffs, sewage disposal and recently illegal oil refining activities. Six stations were selected along the upper reaches of the Nun River across six communities spanning over 50 km. Water, sediment and *E. radiata* samples were collected during the months of August, October, December and January at the established stations. Trace metal (Pb, Cr, Cu, Ni, Cd and Zn) levels, bioaccumulation and bioavailability potentials of the metals in the clam were evaluated. The heavy metal levels were in the order of magnitude *Ergeria*>Sediment>overlying water across all the stations during all the months. Trace metal levels were moderately elevated with Ni recording the highest percentage elevation in the clam. Health implications of consuming seafood with elevated levels of trace metals was assessed and regular assessment of contaminant levels in the Nun River is advocated to avoid severe ecologic and human health impacts.

Keywords: *Trace metals, bioaccumulation, Nun River, Human Health*

Introduction

The Niger Delta is the hub of oil and gas production in Nigeria. It is also Africa's largest wetland and the continent's mangrove dominant region. The exploration and exploitation of oil interfere with ecological and biodiversity integrity of ecosystems arising from flaring of associated gases, oil spills, use of drilling chemicals, etc. These processes can release trace metals into coastal waters (Zabbey and Babatunde, 2015). Oil pollution substantially degrades the delta network of alluvial swamps and lands, creeks and rivers. And there has been growing interest to determine heavy metal levels in the environment (Kalay *et al.,* 1999). Levels of contaminants in fish are of particular interest because of the potential risk to human consumption of fish (Burger & Gochfeld, 2005). Fin and shell fishes have been widely used as bio-indicators to monitor heavy metals concentrations in the coastal environment, due to their wide range of distribution, and also their important position in the food chain.

Oil exploration and exploitation of oil is associated with several operational and accidental spills, use of drilling chemicals, flaring of gases, and burning of fuel that release heavy metals into coastal waters. Pollution studies have revealed elevated levels of Pb, Cr, Ni, V, and Zn in surface water, sediments and some species of fauna, suggesting inputs from petroleum exploration and exploitation (Kakulu & Osibanjo, 1992; Horsfall and Spiff, 2002; Howard *et al.,* 2006; Davies et al., 2004; Chindah et al., 2006; Babatunde et al., 2013; Onojake et al., 2015). Consequently, the concentration of these metals in Nigerian coastal waters and sediment are of great concern, warranting the need for periodic sampling and analyses of both water and water resources in order to monitor the pollution and productivity status of the marine ecosystem and compare the data with international standards (Ajao *et al.,* 1996; Nubi *et al.,* 2008).

Pollution of the littoral waters of the Niger Delta region of Nigeria has in recent times received much attention because of the high degree of environmental degradation and aquatic perturbations posed by petroleum exploration activities in the oil bearing states (Zabbey and Uyi, 2014; Zabbey and Babatunde, 2015). Petroleum hydrocarbons from oil spills and human mediated activities are usually incorporated into sediments where they can persist for years, gradually releasing toxic substances such as heavy metals into the immediate and remote environments (O'Clair *et al.,*1996; Moles and Norcoss, 1998; Zabbey and Babatunde, 2015). Heavy metal distribution in aquatic ecosystems present divergent dynamics depending on such factors as source, flow rates, particle flux rate, sediment characteristics and ecology of organism under study. In the Niger Delta, most reports agree that heavy metal concentrations is low in surface water samples (Davies et al., 2004; Chindah et al., 2006). Sediment on the other hand is believed to be the sink for heavy metals, which usually allow re-suspension anytime the riverbed is disturbed (Babatunde et al., 2013). However, to better characterize the risk presented by metals in the environment to human and ecological receptors, most researchers use benthic organisms as biomonitors of both the levels and long-term influences of heavy metals within an ecosystem (Philips and Rainbow, 1994; Horsfall *et al*., 1998). Several studies have also reported on the safety of seafood in Nigerian coastal waters using fish as bioindicators of bioaccumulation of heavy metals (James and Okolo, 2003; Agbozu *et al.,* 2007), in periwinkle (Davies and Allison, 2006, Davies et al., 2004), Crustacean (Chinda et al., 2004). Unyimadu *et al.,* (2008) reported moderately elevated levels of Cd, Pb, Mn, Zn, Cu, Fe and Cr in different species of finfish from coastal waters at Nun River, Sombreiro River.

Fish remains an important part in the diet of Nigerians, especially for riverine communities such as the inhabitants of the Niger Delta, with seafood being served at almost every meal. Fishing is one of the major occupations of the people of the Niger Delta region and various fisheries resources are important delicacies including *Ergeria radiate* which is popular among artisanal fisheries. The importance of heavy metal contamination of aquatic ecosystems cannot be over emphasised as most of them can bioaccumulate and become significant along the food chain, giving concern of seafood safety to consumers (Davies *et al.,* 2006). Shellfish, especially clams like *E.radiata, Tympanotonus* species are used largely as a condiment in most meals eaten in the Niger Delta and its environs (Gomna and Rana, 2007; Babatunde et al., 2015) and may accumulate metals at levels which can become deleterious to human consumers. Ayenimo *et al.,* (2005), reported elevated levels of some metals in periwinkle from four different markets in the Niger Delta. Similar results have been reported by Davies *et al.,* (2006) for Elechi Creek where the accumulation of three heavy metals; chromium (Cr), cadmium (Cd) and lead (Pb) in periwinkle (*Tympanotonus fuscatus var radula*; shell and soft tissues) was studied. Results showed that sediment concentrated more heavy metals than the overlying water, while the *P. fuscatus* accumulated more of the metals than concentrations measured in sediment.

Bivalves are widely used as bioindicators of heavy metals pollution in coastal waters because they are known to concentrate metals providing indication of the contamination of the environment over time. *Ergeria radiata* as a bivalve has been known to bioaccumulate heavy metals (Ekpo et al, 2015) and thus a useful bioindicator of metal contamination in aquatic environment. For example, Nwanbueze, (2011) reported elevated concentrations of heavy metals in tissues of *E. radiata* from some creeks in Delta State, Nigeria above concentrations in the environment and particularly Pb, Mn and Cd as higher than FAO/WHO acceptable limits of heavy metal contamination in fishes and shell fish. Similarly, Etim, (1990) reported elevated heavy metal contamination in tissues of *E.radiata* from Calabar River, Cross River, Nigeria above the environmental concentrations indicating the animal bioaccumulated the metals. Indeed, numerous studies around the world have demonstrated their ability to concentrate trace elements, even in areas far from anthropogenic sources such as the Antarctic Ocean (e.g., Mauri et al., 1990; Berkman and Nigro, 1992; Viarengo et al., 1993), with seasonal variations in the concentrations at various stages of their lives (Bryan, 1973) and in the Bay of La Rochelle in France (Bustamante and Miramand, 2005).

Bioaccumulation can be defined as the net accumulation of a metal in a tissue of interest or a whole organism that results from exposure. Metal bioaccumulation can apply to the entire organism, including both metal adsorbed to surfaces or absorbed by the organism, or to specific tissue; it is usually expressed on a weight (dry or wet) adjusted basis (McGeer *et al.,* 2004). The bioaccumulation of metals arises from multiple environmental sources including air, water, solid phase (organic and inorganic phases in soil and sediment), and diet. Bioaccumulation that occurs under steady-state conditions (i.e. where accumulation remains relatively constant because uptake is offset by elimination) is often of primary concern in risk assessment. Bio-concentration factor (BCF) is the ratio of metal concentration in an organism to metal concentration in water (McGeer *et al.,* 2004). Metal concentrations are usually expressed on a weight-adjusted whole organism basis and waterborne metals as total metals. In the broadest context, the bioaccumulation factor (BAF) is the ratio of metal concentration in an organism to that in the surrounding medium, at steady state.

This relationship is much more complex than presently evaluated in most reports on heavy metal bioaccumulation which accounts for the ratio of only uptake and environmental concentrations. Steady state bioaccumulation models must also properly account for the fate of the metal consumed with respect to assimilation and elimination and compartmentalization of the metal in the organism's body parts. Biomagnification of heavy metals in edible tissues of some shellfishes, for example, *Tympanotonus* sp. *Pachymelania* sp., *Littorina* sp., *Pugilina* sp. from the Niger Delta area have revealed heavy burdens (Kakulu *et al.*, 1987; Dambo and Ekweozor, 2000; Oronsaye, 2000). The bioavailability and bioaccumulation properties of inorganic metals in sediments and aquatic systems are complex. Modifying factors such as metabolism, assimilation and solubility of the metals determine the concentration of metals that interacts with biological surfaces (e.g. gill, gut, or root tip epithelium) and binds to or absorbed across these membranes (McGeer *et al.,* 2004).

The freshwater clam, *E. radiata,* also called River oyster or Volta clam, is endemic to the Volta River in Ghana and some southern Nigerian rivers, particularly common Itu River in Cross River State (Edmunds, 1978; Yoloye, 1988). The clam is also exploited in artisanal fisheries for food in the Nun River basin in the Niger Delta. In this report, a steady state bioaccumulation model that incorporated all the aforementioned ratios was used to arrive at the most probable bioaccumulation factor in the freshwater clam, *E. radiata,* from the Nun River. This will, most potently, elucidate potential health hazard that may arise from consuming the clam from the study area and provide insights that will moderate human consumption patterns of the clam, and regulatory enforcement for integrated catchment management of the resources of the study area.

Materials and Methods

Study Area

The present study was carried out at six stations in the tributary of River Nun that runs along communities within Southern Ijaw Local Government Area of Bayelsa State, Nigeria. The study area was a transect spanning a distance of over 50 kilometres of the upper reaches of the river. Within the area, the river drains and receives effluents from the activities of oil companies drilling for oil and commercial boat drivers. The river also serves as sewage/rubbish disposal medium for the surrounding communities, in which they also do most of their laundry along the riverbanks. The river is also, in recent times, "home" to the activities of illegal artisanal refineries and also a receptacle of runoffs from the surrounding agricultural fields. The climate of the area is typically tropical with dry (November-March) and wet (April-October) seasons. Rainfall is bimodal, peaking usually in July and again in September with a brief drop in August. Minimal rainfall is in January and February, followed by the onset of heavy rainfall in April. Annual temperature ranges from 22 - 32^{oC}, while annual humidity is between 69 and 96% (NIMET, 2010).

The sampling stations with their coordinates are: Ogbonogbene (Station 1) N04^{0} 53' 17.8" E 006^{0} 53' 58.3", Umbugbene (Station 2) N04^{0} 48' 06.9" E 006^{0} 01'04.2", Ondewari (Station 3) N04^{0} 46' 14.0" E 006^{0} 00' 24.2", Korokorosei (Station 4) N04^{0} 45' 19.8" E 006^{0} 00' 54.4", Ogbainbiri (Station 5) N04^{0} 50' 00.8" E005^{0} 58'40.0", and Ogbainbiri (Station 6) N04^{0} 49'17.7" E 005^{0} 57'51.4" (Figure 1). There are oil wells being currently drilled for oil at stations 5 and 6.

Sample Collection

This study was conducted between August 2013 and February 2014. Sampling was done bi-monthly.

Collection of Water Sample

Composite water samples made up of 10 grab samples of 250 ml were collected from each station in clean sterilized plastic bottles treated with 10% nitric acid. In the field, plastic bottles were rinsed with sample water before filling to the brim at a depth of about half a meter below the water surface. The labelled bottles were covered under water and put in an ice-chest and taken to the laboratory the same day for heavy metal analysis.

Collection of *Ergeria radiata* samples

Matured *E. radiata* specimens were collected directly from the river at each sampling station with the help of fishermen who harvested the shellfish by diving. They were then put in plastic containers with ice, labelled and taken to the laboratory the same day and refridgerated for further analysis. An average of five animals were taken per station on each sampling date.

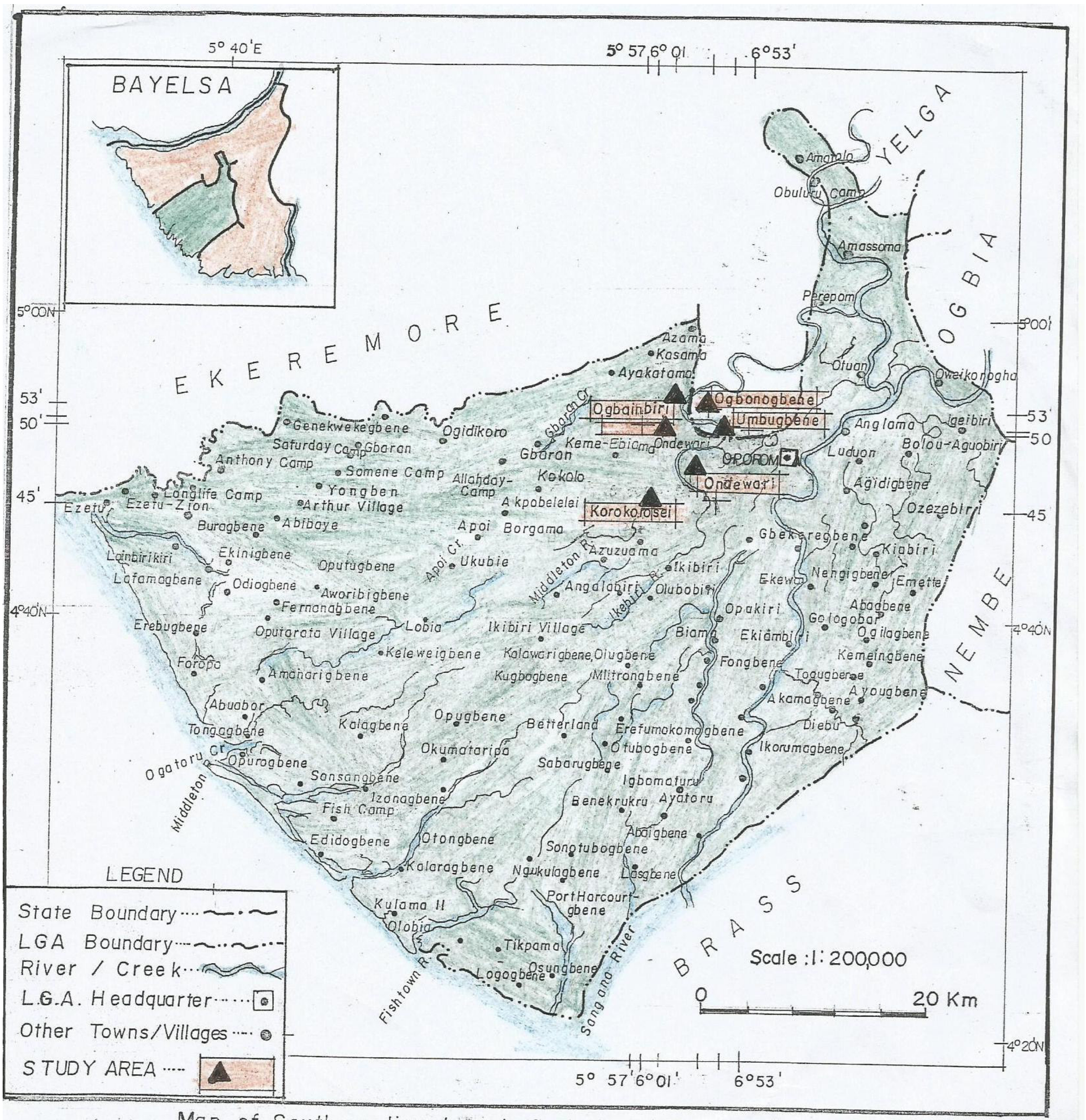
Collection of Sediment Sample

At each station, replicate sediment samples were collected from three different spots using a sterile plastic container pretreated with 10% nitric acid. The replicate samples were then put together, harmonised into a composite sample and stored in labelled plastic bags and taken to the laboratory on ice chest. A total of twenty four sediment samples were collected.

Sample Preparation

Sample Digestion

The method described by Allen *et al.,* (1974) and APHA, (1998) were used. Few drops of water was added to 10 g portion of the sediment or biota samples to wet it in a 100 ml beaker. Thereafter, 2 ml perchloric acid, 4 ml nitric acid, and 1 ml sulphuric acid were added and the sample was slowly digested for one hour. More acids was added until a clear solution was obtained. The completely digested samples were allowed to cool at room temperature, diluted using 1.5 M HCL acid and filtered through a 0.45 µm membrane filter and the volume made up to 50 ml in volumetric flasks with double distilled water (Jin *et al*., 1999; Sastre *et al*., 2002). All digested samples were analyzed three times for the metals using AAS (Varian Spectre AA 200 Fast Sequential Flame Atomic Absorption Spectrometry). The instrument was calibrated with standard solutions prepared from Merck. The analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid matrix (Türkmen, 2003). The accuracy and precision of our results were checked by analysing standard reference material (SRM, IAEA-360 Mediterranean sediment). All metal concentrations were quoted as mg kg-1 dry weight unless otherwise stated. All chemicals and standard solutions used in the study were obtained from Merck and were of analytical grade. Doubled distilled water was used throughout the study. All glassware and other containers were thoroughly cleaned with 10% (w/v) nitric acid solution and finally rinsed with double distilled water several times and air dried prior to use. One-way analysis of variance (ANOVA) and Duncan's test ($p=0.05$) were used in order to access whether heavy metal concentrations varied significantly between sites and species. The probabilities less than 0.05 ($p<0.05$) were considered statistically significant. All statistical calculations were performed with SPSS 9.0 for Windows.



Map of Southern Ijaw Local Govt. Area Showing Sample Collection points

Fig.1: Map of Southern Ijaw LGA in Bayelsa showing sample locations with black triangles

Steady State Bioaccumulation (BCF) and Bioavailability (BAF) Models

A variety of different modelling approaches exist for understanding bioaccumulation and bioavailability of contaminants. The BCF and BAF represent a single compartment model (Baron *et al.,* 1990; Newman, 1995) that predicts partitioning between the exposure medium (water in this example and sediment) and the biota. BCF and BAF are generally calculated as the ratio, at steady state, of internal biota concentration to exposure concentration. Although the calculation of BAF and BCF are the same the interpretations are slightly different, with accumulation in organisms arising from water only for BCF and from water and dietary sources for BAF. Therefore, in general, BAF is derived from measurements in natural environments, and BCF is more readily measured under laboratory conditions.

The BAF and BCF model is among the most simplified models of bioaccumulation. BAF and BCF were developed with as well as conceptually mechanistically validated for neutral hydrophobic organic substances (Holden, 1962; Neely *et al*., 1974; Branson *et al.* , 1975; Krzeminski *et al.* , 1977; Veith *et al.* , 1979; Erikson and McKim, 1990; Kenaga, 1980; Baron, 1990; Feijtel *et al.,* 1997; Meylan *et al.* , 1999). In fact, the success of the BAF and BCF model as valid indicators of the environmental and toxicological behaviour of neutral organic substances is due to their hydrophobic/lipophilic chemical properties, and this has important consequences for application to inorganic metals and their consequent transfer along the food chain.

At the core of the BAF/BCF model is the assumption that accumulation is described by rate constants for uptake and elimination, including physiological excretion as well as metabolic breakdown and natural degradation/depuration. The relationships for uptake and loss are shown in the equation below, where "C" refers to the concentrations of a substance in either the fish or water, "K" is the rate constants for either uptake or depuration, and "t" is exposure time (Branson *et al.* , 1975; Veith *et al.* , 1979).

$$C_{fish} = \frac{K_{up}}{K_{dep}} * C_{water} * (1 - e^{-(t*K_{dep})})$$

At steady state the term $e^{-(t*kdep)}$ goes to zero and therefore the above equation simplifies and rearranges to the equation below, illustrating that BCF and BAF are equivalent to the ratio of uptake to depuration rates (Newman, 1995).

$$\frac{C_{fish}K_{up}}{C_{water}} = \frac{C_{water}K_{dep}}{K_{dep}}$$

This Bioenergetic-based kinetic model was summarised for the present study as shown below and used to determine bioaccumulation and bioavailability of the metals to higher trophic levels and determine relative contribution of water and sediment to the metal load in the animal.

$$Css = \frac{C_f - AE.IR}{Ke,_f + g} \quad x \quad \frac{1}{Ku_w.C_w + Ku_s.C_s}$$

Where:
Ku & ke= uptake and elimination rate constants
C_f, C_{SW}, C_S = concentrations in seawater and sediments
AE= assimilation efficiency
IR= ingestion rate
g= growth rate

Results and Discussion

Heavy metals in water samples

Result of mean monthly concentration of heavy metals in the Nun River water samples is shown in Figure 2. In August, Cd was below detection limit but Zn, Ni, Pb, Cr and Cu recorded 1.2, 0.04, 0.03, 0.09 and 0.19 mg/L, respectively. In October, Cd and Pb were below detection limit while Zn, Ni, Cr and Cu had concentration of 0.07, 1.52, 0.08 and 0.03, respectively. In December, Pb and Cr were below detection limit, Cd and Ni recorded 0.01 mg/L, respectively, while Zn and Cu recorded 0.7 and 0.05 mg/L, respectively. In January, Cd and Ni were below detection limit, while Zn, Pb, Cr and Cu recorded 1.04, 0.03, 0.03 and 0.05 mg/L, respectively.

Globally, heavy metal accumulation in the aquatic environment is of great concern because of their toxicity to the ecosystem and man (Ekpo et al, 2015). Metals such as Cu and Zn are generally regarded as essential trace metals because of their valuable role in metabolic activities in organisms. However, metals like Cd, Pb, Ni and Hg exhibit extreme toxicity even at trace levels (Merian, 1991). Several workers have investigated the concentration of heavy metals in Nigerian waters. A good account of such studies in the Niger Delta is given in the work of Asonye *et al.* (2007) in which heavy metal load of several rivers in Nigeria is reported. Generally, low concentration of heavy metal have been reported in Nigerian water bodies by earlier workers, notable among which are Obire *et al.,* (2003) on Elechi Creek, Chindah *et al.,* (2004) on lower Bonny River, Omoigberale and Ogbeibu (2005) on Ase River, Southern Nigeria. Others include the reports of Abu and Egenonu (2008) on the New Calabar River; Asonye et al., (2007); Chindah *et al.,* (2004); Ubalua *et al.,* (2007); Vincent-Akpu and Babatunde, 2013;Vincent-Akpu *et al.,* 2015). Although the results of surface water concentrations of heavy metals observed in the present study agrees with the general opinion of low levels of heavy metal in surface water, some of the toxic metals having concentrations higher than WHO (2006) stipulated limits require continuous monitoring to detect malicious increases to avert possible public health implications.

According to Freedman (1989), the chemical form of toxic elements dissolved in water is generally relatively available to biota, even seemingly small aqueous concentration may exert powerful toxic effect.

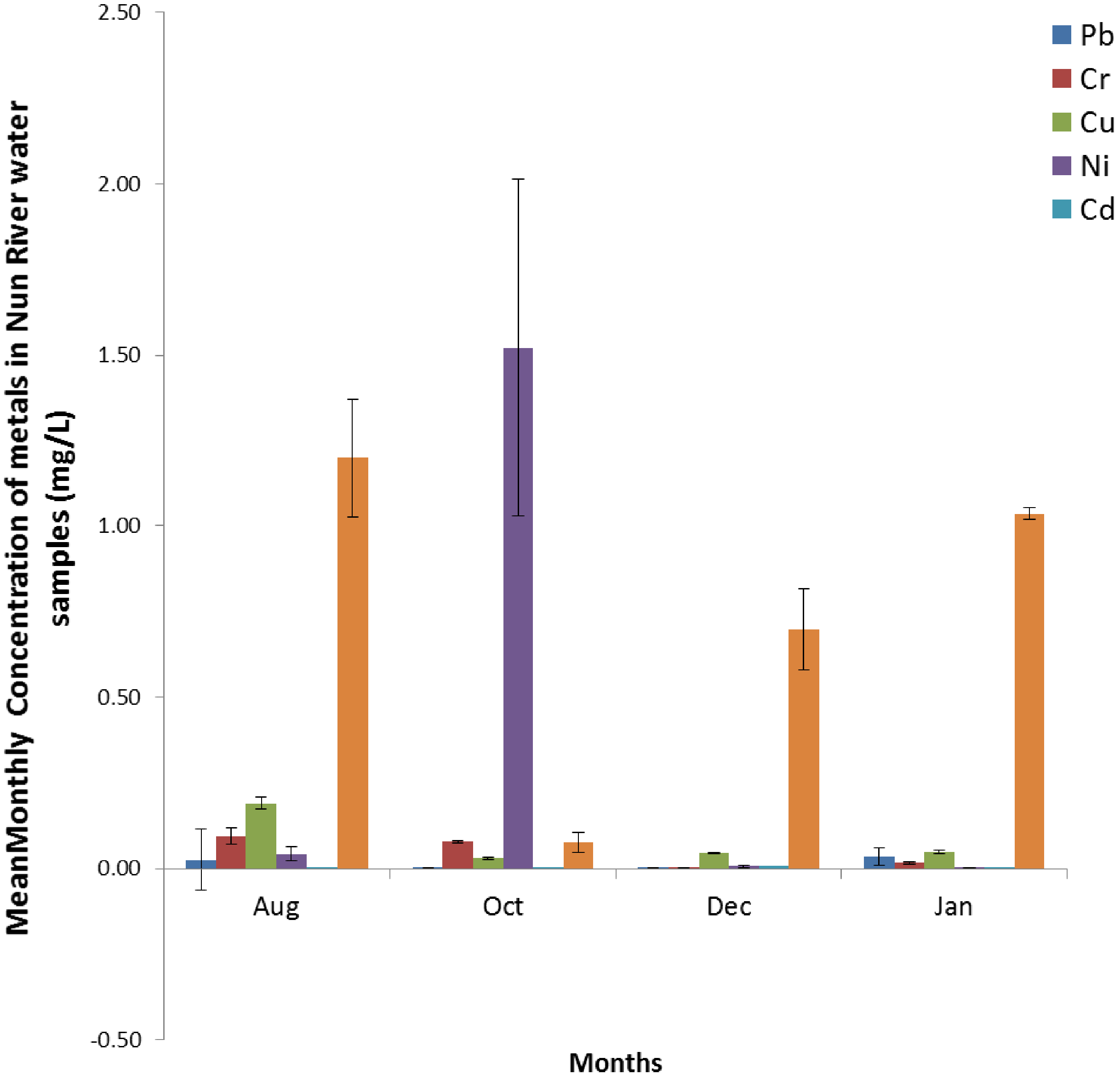


Fig. 2: Mean Monthly concentration of heavy metals in Nun River water samples between Aug –Dec 2014 and Jan 2015 (n=12)

Heavy metals in sediment samples

Mean concentrations of heavy metal load of the Nun River sediment is presented in Figure 3. Lead and Cd were below detection limit in all the studied months, except in August when Pb was 0.39 mg/kg while Cr, Cu, Ni and Zn recorded 0.21, 0.36, 0.21 and 0.55 mg/kg, respectively. In October, Cr, Cu, Ni and Zn recorded 0.20, 0.17, 4.38 and 0.78 mg/kg, respectively. In December, Ni was below detection limit, while Cr, Cu and Zn recorded 0.04, 0.09 and 1.39 mg/kg, respectively. In January, Ni was below detection limit, while Cr, Cu and Zn had values of 0.05, 0.06 and 0.99 mg/kg, respectively. Sediment represents the most important sink for heavy metals in aquatic environments because more than 90% of heavy metals load in marine sediments is bound to suspended particulate matter or sediments (Daskalakes and O'Connor, 1995; Calmano *et al.,* 1993).

Heavy metals accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds (Ankley *et al.,* 1992; Leivouri, 1998). These metals could enter the aquatic environment through natural sources which involve weathering of minerals and soils or from anthropogenic source (Daskalakes and O'Connor 1995; Merian, 1991; Komarek and Zeman, 2004). Weathering associated with the release of heavy metals is of environmental importance because they can serve as either natural contamination sources or soil nutrient input. The concentrations of natural metals in estuarine sediments depend on the geology of the area (Windom *et al.,* 1989). Anthropogenic inputs are mainly from domestic sewage, industrial effluent, traffic emissions or from mining and refining operations (Merian, 1991; Kabala and Singh, 2001; Chindah *et al.,* 2004). The sediments serve as metal pool that can release metals into the overlying water through bioturbation and dredging, causing potential adverse health effects of human life and ecosystem (Daskalakis and O'Connor 1995; Argese *et al.,* 1997; Fatoki and Mathabatha, 2001, Kishe and Machiwa, 2003; McCready *et al.,* 2006). Marine organisms or biota can take up heavy metal from the environment through pathways (contact and food intake), which in turn increases the potential of some metals entering into the food chain (Chen *et al.,* 2007).

The present study showed heterogeneous distribution of heavy metals concentration in sediment of the Nun River, without detectable pattern or seasonality. This could be attributable to the dynamics of the river system, characterized by factors such as haphazard flow rates, reversal effects and high mixing reported (Richard, *et al.,* 1997; Tamia, 2001; Seiyaboh *et al.,* 2013). Zn was detected at all stations in all the months of study but recorded the highest concentration in December followed but October. Cu was also detected at all stations in all the months of the study but had its highest concentration at station 5 followed by station 6 in the month of August. Pb was detected at all the stations in the month of August except station 4 but was below detection limit in the sediment in all other months except in January at stations 5 and 6. Cd was below detection limit at all stations in all the months except in December when it was detected at stations 3, 4, 5 and 6. Ni was detected at all stations in the months of August and October except at station 3 in August and 4 in October when it was below detection limit. Ni concentration in sediment was the highest in the present study.

The results of heavy metal concentrations recorded in sediments of the Nun River were lower than those reported for the same river by previous workers Uyimadu *et al.,* (2008), and lower than reports from envronment in the Niger Delta region (Faboya *et al.,* 2012). Yet the data recorded conform with the findings of others (Davies *et al.,* 2006). Compared with concentrations in Asonye *et al.,* (2007), the values were generally lower than concentrations recorded at Kayama I and II, Odi River and Okosi River in Bayelsa State.

In the present study, all the metals assessed had concentrations higher in sediments than in surface water (Fig). However, only Zn, Ni and Pb recorded higher concentrations in sediment than surface water at statistically significant level (P = 0.035). Some studies have reported similar results for the metals examined to recorded higher concentrations in sediment than in surface water in the Bonny/New Calabar Estuarine system of Niger Delta (Chindah *et al.,* 2004; Uyimadu *et al.,* 2008). However, the results obtained in this study for heavy metal concentrations in sediments were higher than that of other studies in the Niger Delta (Davies *et al.,* 2006; Horsfall and Spiff 2002; Iwegbue *et al.,* 2007; Obire *et al.,* 2003).

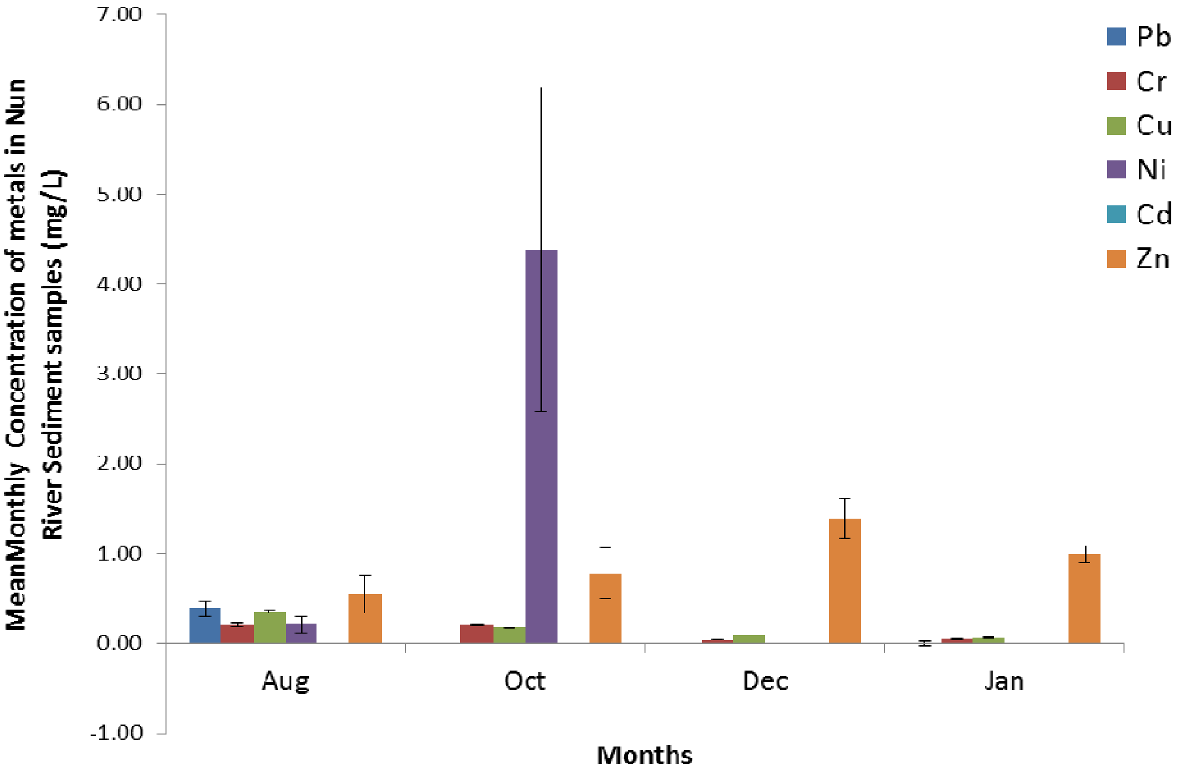


Fig. 3: Mean monthly Concentration of heavy metals in Nun River sediment samples (n=12)

Heavy metals concentrations in *E. radiata* in the Nun River

Results of heavy metal analysis in the river clam, *E. radiata* are presented in Figures 4 for wet and dry season, respectively. The concentration of heavy metals in *E.radiata* from the Nun River was in the magnitude Zn>Cu>Cr>Pb>Cd>Ni with wet season mean values of 3.28±, 0.56±, 0.40± and 0.15±, mg/kg for Zn, Cu, Cr and Pb respectively while Ni and Cd were below detection limit of the equipment in all wet season samples.

In dry season, Zn mean concentration was 2.42±0.77 mg/kg in the edible part of the clam, Cu recorded mean value of 0.58±0.21mg/kg in the clam. Cr concentration was 1.05±0.5 mg/kg in the clam. While, Pb was not detected in the clam, Ni and Cd recorded mean concentration values of 0.78±0.32 mg/kg and 0.03±0.01 mg/kg respectively.

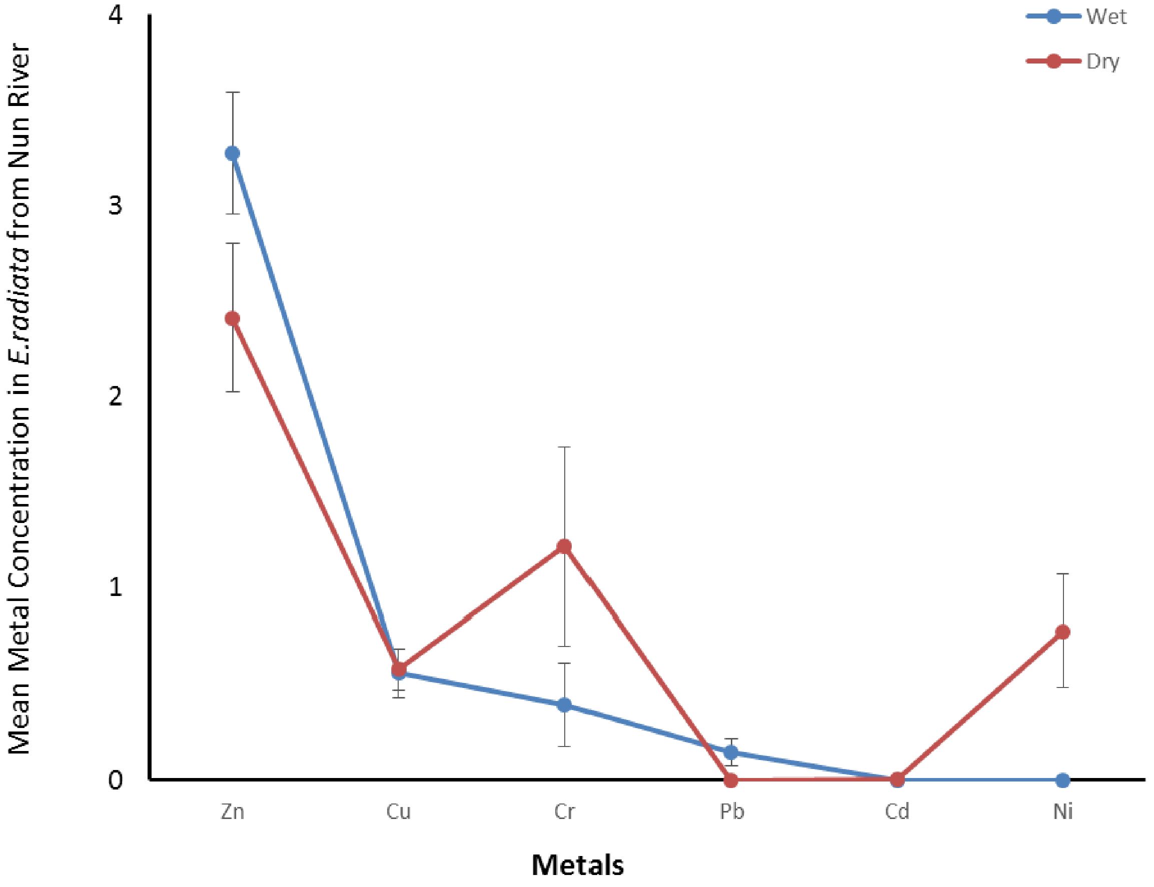


Fig. 4: Wet and Dry season concentration of heavy metals in *Ergeria radiata* from the Nun River (n=12).

Bioaccumulation

Results of the bioaccumulation of metals from water and sediment of the Nun River by *E. radiata* is shown in Table 4. The percentage elevation of metals in *E. radiata* when water was the medium was 10.5% for Pb, 2.95% for Cr, 6.94% for Cu, 67.01% for Ni, 24.48% for Cd and 13.21% for Zn. When sediment was the medium, metal concentration elevated up to 65.96% for Pb, 7.75% for Cr, 14.97% for Cu, 196.10% for Ni, 54.20% for Cd and 16.29% for Zn. Higher metal concentration when sediment was the medium was due to the biology of *E.radiata* which lives buried most times under the sediment filtering its food. Similar bioaccumulation results have been reported by Davies *et al.* (2006) of heavy metals in water, sediment and periwinkle (*Tympanotonus fuscatus* var. *radula*) from Elechi Creek, Niger Delta. They noted that the sediment concentrated more heavy metals than water, while periwinkles accumulated more of the metals determined than the sediment. Sediments have been reported as the major repository of heavy metals in aquatic systems (Olowu *et al.,* 2010). Aquatic organisms such as fin fish and shellfish whose biology revolves around the sediment usually accumulate heavy metals at concentrations through the processes of biosorption and magnification many times higher than the concentrations in the surrounding water or sediments (Olaifa *et al.,* 2004). Humans who then consume such seafoods with elevated levels of heavy metals stand high risk of suffering serious health hazards associated with toxic levels of the metals (Peul *et al.,* 1987; USEPA., 1991; Anadon *et al.,* 1984; Birge *et al.,* 2000). Industrial and domestic effluent constituted the largest sources of heavy metal, which contribute to increasing metallic contaminant in aquatic environments in most parts of the world (Olowu *et al*, 2010; Wangboje and Oronsaye*,* 2001). Several reports have reported elevated levels of heavy metals in aquatic organisms especially bivalves several folds their concentrations in the environment.For example, Onwumere and Oladimeji (1990) reported 1000 fold accumulation of heavy metals in *Oreochromis niloticus* exposed to treated petroleum refinery effluent.

Results of the bioaccumulation of metals in the present study from water and sediment of the Nun River by *E. radiata* was in the order of magnitude Ni<Pb<Cd <Zn<Cu<Cr in relation to water as the medium and Ni< Cd<Zn<Pb<Cu<Cr in relation to sediment as the medium with Cr and Ni recording the highest and least bioaccumulation factor in each case. On the other hand, the magnitude of the proportion or percentage of metal elevation in *E. radiata* was in the order Ni>Cd>Zn>Pb>Cu>Cr in relation to water as the medium and Ni>Pb>Cd>Zn>Cu>Cr with Ni recording the highest in each case measuring up to 196.10% elevation in the clam in relation to sediment as the environmental medium. The least elevated concentration was that of Cr having 2.95%. Babatunde *et al.,* (2013) reported the order of magnitude of accumulation of metals in fish as Co>Cr>Ni>Mg>Zn>Pb>K>Na>Ca>Cu>Cd>Fe and in crab Ni>Pb>Co>Cd>Cu>Mg>K>Cr>Na>Fe>Zn>Ca, showing crab closer to the sediment accumulates Ni most as reported in the present study. Some of the metals such as Ni, Na, Fe, Cu, Cd, and Pb were better accumulated in crab with three times more Ni in crab than in fish as confirmed the present study. However, some of the metals such as Cr, Co and Zn were better bioaccumulated in fish than in crab. Bioaccumulation of metals was generally higher in both organisms when sediment was the medium of evaluation with metals such as Zn, Fe and Ni bioaccumulating in the magnitude of 10, 6 and 5 times higher in the organisms. This may be as a result of higher metal concentrations in sediment and the biology of the organisms studied, which typifies bottom feeding habits (Babatunde *et al.*, 2013).The mechanism of bioaccumulation of metals vary with each species of organism and the type of metal in question as opinied by Babatunde et al., (2013) and the modelling of such mechanisms for each metal in several species of organisms would elucidate and provide better understanding of the bioaccumulation process. Similar results have been reported for Pb, Cr, and Cd in some fin fishes which were found to be moderately elevated at 50%, 37.1%, and 35% of the samples, respectively, as reported by Uyimadu *et al.* (2008). However, the present result disagrees with Uyimadu *et al.,* (2008) for Zn, and Cu which exhibited no discernable elevation in their report. The results also differ from those reported by Chindah *et al.,* (2006) and Jamabo (2008) for the same metals in a periwinkle, *T. fuscatus* from the Bonny River, Niger Delta.

The rate of bioaccumulation showed different patterns for the different media. Even in the medium, different metals may bioaccumulate differently and there may be specific or confounding factors influencing selective bioaccumulation of metals in the organism. However, according to Eneji *et al.* (2011). The rate of bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to digest the metals and the concentration of the metal in the ambient environment. Also biological metal load is also dependent on feeding habits. Furthermore, some of the factors may include, age of fish and lipid content of the tissue are significant factors that affect the accumulation of heavy metals in fishes (Chindah et al. 2009). Some studies conducted in Nigeria had reported metal bioaccumulation patterns similar to this study in different organisms in the Bonny/New Calabar River Estuary (Chindah et al. 2009; Davies et al. 2006), and River Benue (Eneji *et al.,* 2011).

Heavy metals have multiple effects on biological systems depending on the oxidation state, the formation of complexes and biotransformation of elemental species. Health effects of heavy metals such as Pb, Zn, Cr, Cd and Cu in humans have been demonstrated in acute toxicity, neurotoxicity and nephrotoxicity (Katz and Salem, 1993; ATSDR 200; Stift *et al.,* 2000; WHO 2011), while Pb is a confirmed carcinogen (Martin and Griswold, 2009; WHO 2011). Some observed effects of Ni in aquatic environments include tissue damage, genotoxicity and growth reduction in organisms. Molluscs and crustaceans are more sensitive than other aquatic fauna (Onojake and Frank, 2012).

Table 4.5.1: Bioaccumulation factors and percentage elevation of metals in *E. radiata* from the Nun River.

Metals	CF (Water as the Medium)	% Elevation	CF (Sediment as the Medium)	% Elevation
Pb	1.52	10.50	9.52	65.96
Cr	12.91	2.95	33.87	7.75
Cu	6.68	6.94	14.41	14.97
Ni	0.51	67.01	1.49	196.10
Cd	1.85	24.48	4.09	54.20
Zn	6.14	13.21	7.57	16.29

CF = Concentration Factor

Conclusion

Steady state bioaccumulation model applied in the present study is a holistic and potent estimate of bioacmulation factor with respect to heavy metals concentration in aquatic organisms because it considers all sources of the pollutant in proportions. The study demonstrated that sediment contributed more to heavy metals load in the clam and the percentage elevation of the heavy metals was haphazard with Ni recording the highest percentage elevation when compared to both water and sediment samples. The danger of consuming the clam *E.radiata* studied here is explicit as shown in its ability to concentrate metals from the environment with high potential to transfer same along the food chain.

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