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HEAVY METAL POLLUTION OF SEAWATER, SEDIMENT AND SHRIMPS OF QUA IBOE RIVER, IBENO, AKWA IBOM STATE, NIGERIA

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ABSTRACT: Heavy metal pollution of seawater, sediment and shrimps of Qua Iboe River, Ibeno, Akwa Ibom State, Nigeria was studied for six months in dry and wet seasons. Seawater, sediment and shrimp samples were collected from five different points from the upper to the lowest course of Qua Iboe River flowing along Mkpanak Community. Heavy metals (Pb, Cu, Cd, Cr and Ni) concentration in seawater, sediment and shrimps from the studied river were determined using Atomic Absorption Spectrophotometric (AAS). The mean concentrations of heavy metals in seawater were 0.628, 0.072, 0.381, 0.486 and 0.631mg/l for Pb, Cu, Cd, Cr and Ni respectively for dry season and 0.427, 0.049, 0.214, 0.289 and 0.408mg/l for Pb, Cu, Cd, Cr and Ni in wet seasons. The corresponding values in the sediments were 3.552, 1.327, 2.578, 2.829 and 4.926mg/g for Pb, Cu, Cd, Cr and Ni respectively for dry season and 2.121, 0.943, 1.517, 1.777 and 3.675mg/g for Pb, Cu, Cd, Cr and Ni respectively in wet season. Also, the mean values of heavy metals in shrimps were 0.008, 0.308, 0.004, 0.039, 0.025mg/g for Pb, Cu, Cd, Cr and Ni respectively for dry season and 0.005, 0.196, 0.002, 0.020 and 0.017mg/g for Pb, Cu, Cd, Cr and Ni respectively in wet season. The results of heavy metals in seawater, sediment and shrimps were compared with International Standards. It was observed that all the heavy metals studied in both seasons were above the safe limit with exception of Ni in shrimp which was within the safe limit. Hence, this study recommended the need for appropriate regulatory legislation on the control, treatment and discharged of oilfield effluents into Qua Iboe River.

KEYWORDS: Heavy Metals, Seawater, Sediment, Shrimps, Qua Iboe River

INTRODUCTION

Pollution of water body has become a major problem in developing nations of the world, where lagoons, rivers, and streams have become sinks for wastes. Wastes are most often discharged into the receiving water bodies with little or no regard to their assimilative capacities. These discharges into the water body affect the physicochemical properties of the receiving water body. Raw effluents discharge into River Challawa in Kano resulted to high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Wakama et. al., 2008). The rivers themselves are now considered an environmental health hazard due to the high concentrations of chemical and bacteriological pollution and nearly half of the urban and rural population are at one time or the other, dependent on them as a source of water for domestic use and in worst cases for drinking.

Influent seepage of urine and leachate from polluted surroundings such as pit latrine (which are very common in developing countries) or soak-away sited upstream could also enrich surface waters with contaminants (Okoye, 1991). Effluent discharged into water bodies leads to accumulation of contaminants such as heavy metals, organometallic or persistent organic pollutants (Ridgwa and Shimmield, 2002). These contaminants become distributed between the aqueous and solid phases of the water bodies. According to Piont et. al., (2007), the sediment is well recognized as an important sink for the compounds present in the upper water column, through the deposition and the burial of suspended particles. On the other hand, the occurrence of bio-turbation and re-suspension processes, currents and waves, dredging and other anthropogenic activities may enhance the remobilization of these compounds at the sediment-water interface, thus resulting in bio-accumulation and bio magnification processes along the whole tropic chain. These contaminants, according to David and Johanna (2000) may adversely affect the physical, chemical, and biological characteristics of the water.

Heavy metals could enter the aquatic environment from both natural and anthropogenic sources. Natural sources include weathering of rocks and soils (Merian, 1992). Anthropogenic inputs are mainly from industrial effluents, domestic effluents, water runoffs and spoil heaps (Agbozu and Ekweozor, 2001). In water bodies, heavy metals may become bound to silt particles, mixed with compounds and settle to the bottom or become absorbed by sediments (Oboh and Edema, 2007). They may be ingested by sea animals or absorbed by sea plants and thus enter food chain where they bioaccumulate. Several authors have reported on the pollution status of some aquatic resources in Nigeria (Obodo, 2001; Ezeronye and Ugbogu, 2004).

Ibeno Local Government Area is a coastal sub-region characterized by abundant water resources. The absence of potable water supply for domestic use in some parts of Ibeno has compelled the population to rely heavily on natural sources of water supply for domestic uses. The qualities of most of these sources of water supply are doubtful, but people in most parts of the area drink from these sources and use these waters without treatment or having regards to the quality. The anthropogenic and natural phenomenon seems to affect water quality in the study area. These include environmental hazards such as gas flaring, oil spillage, and then washing of materials with detergents into water bodies, wastewater and sludge from industrial processes, poor sanitation, storm surges, salt water extrusion and intrusion, sanitary sewer lines. One of the deadliest and wide spread pollutants of water are heavy metals, untreated human waste and sewage released into waterways. This forms the major causes of illness and death in developing countries. The progressive and irreversible accumulation of these metals in various organs of marine creatures ultimately leads to metal related diseases in the long run because of their toxicity, thereby endangering the aquatic biota and other organisms (Hart, 1982). According to the scholars, (Usman et. al., 2012), heavy metals become toxic in human when they are not metabolized by the body and accumulate in the soft tissues causing health problems.

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MATERIALS AND METHODS

Study Area

The area under study is Mkpanak village, located in Ibeno Local Government Area of Akwa Ibom State. Ibeno Local Government Area lies on the eastern side of Qua Iboe River between latitudes 4.30^0 and 4.45^0N and longitude 7.30^0 and 8.0^0E (Figure 1) and is one of the largest fishing settlements on the Nigerian coast (Andem et. al., 2013).

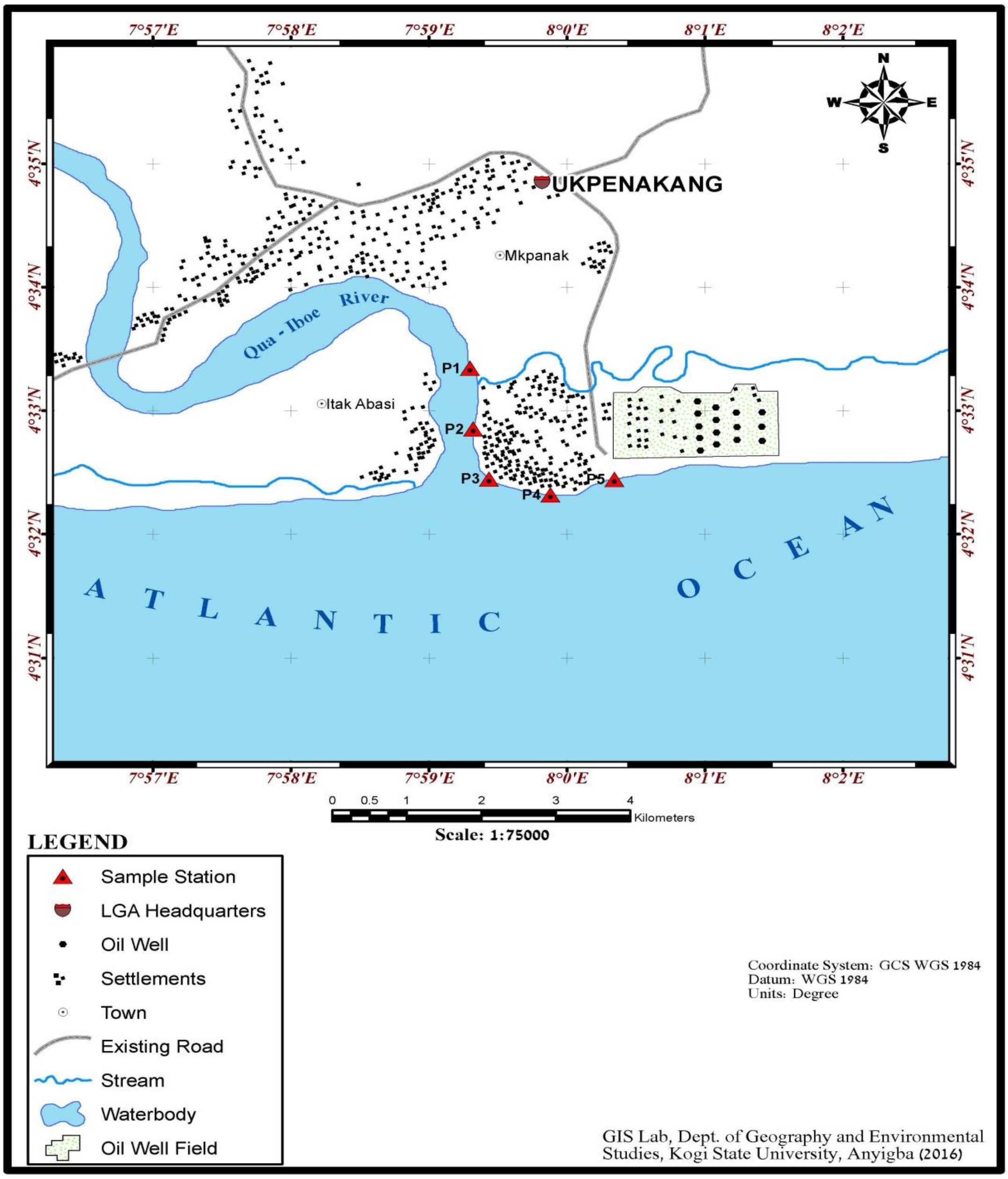

Figure 1: Map of Qua Iboe River Showing the Sample Stations

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It has a coastal area of over 1,200 square kilometers with the population of 74, 840 (National Population Commission, 2006). The Ibeno clan consists of twenty-three villages; it stretches for about forty kilometres from Ikot-Abasi in the West to the mouth of Cross River in the East. It is bordered by Oron and Eket East in the North East and by Eket Central and Oniong Eket in the North West, as well as by the Atlantic Ocean in the South. Ibeno is divided into two sub areas by the Qua Iboe River. The area across the river is made up of six villages. Most of the villages are further separated from one another by small creeks and marshland. The original thick mangrove swamp is giving way in some places to scanty bushes due to the effect of pollution.

The communities on the west bank of the Qua Iboe River do not have access to the hinterland except by boat through the river and creeks. The notable creeks are the Stubbs and Douglass which forms one of the major tributaries of the estuary. Petroleum exploration and production (E&P) waste from the Exxon Mobil Qua Iboe Terminal (QIT) tank farm are transferred to the lower Qua Iboe River Estuary and adjourning creeks through two 24" diameter pipes (Dan et. al., 2014). The Exxon Mobil oily sludge dumpsite is located adjacent to the creek and the stack where gas is flared continuously is also situated a few meters from this creek (Dan et. al., 2014). Some communities such as Mkpanak, Upenekang, Iwuoachang, Okorutip Atasi and Qua Iboe Terminal (QIT) are located on the bank of the Qua Iboe River.

Collection of seawater sample

Seawater samples were collected from five different sampling points along the long profile of Qua Iboe River. The samples were collected in triplicate into plastic bottles and acidified to pH of 2 by adding concentrated HNO_3 ($5cm^3$) to 1 litre of the sample to ensure that element are present in only one oxidation state (ASTM, 1999). The plastic bottles were initially washed with the water to be collected and finally washed with distilled water before sample collection. The samples were immediately taken to the laboratory for heavy metal analysis.

Collection of sediments

The sediment samples were obtained from five sampling points along the study River using hand trowel (Polprasert, 1982). The hand trowel was used to scoop the inner sediment into black polyethylene bags with labels. The sediments were acidified to suppress the growth of micro-organisms.

Collection of shrimp samples

Shrimp samples were collected from the local fishermen engaged to catch them using shrimp traps at the required sampling points. The shrimp samples were collected alive.

Digestion of water for heavy metal analysis

About 100ml of the water sample was filtered using a whatman filter paper No. 1. The filtrate was acidified with 10ml Analar nitric and 10ml of 50% HCl solution. It was evaporated to near dryness on an electric hot plate. After cooling, the solution was quantitatively transferred to 100ml volumetric flask and made up to the mark with deionized water and the metals determined by the use of Atomic Absorption Spectrophotometer, UNICAM 939/959.

RESULTS AND DISCUSSION

Heavy metals in seawater from Qua Iboe River

The concentrations of heavy metals in the seawater from Qua Iboe River, sampled in two seasons from five points of the river are presented in Table 1. The values in the dry season decreased according to the following trend: Ni > Pb > Cr > Cd > Cu, while the trend for the wet season was Pb > Ni > Cr > Cd > Cu. The values recorded for the dry season were significantly higher ($p < 0.05$) than the values obtained for the wet season. The findings in this study revealed that the mean concentrations of all the metals studied in both seasons were significantly higher than the maximum limits set by WHO (2003) [Table1]. The mean concentration of copper during wet season, 0.049mg/l was within 0.05mg/l maximum limit recommended by NESREA (2009). The result of heavy metals investigation in this study is consistent with the reports of Bassey (2015) and Onuoha and Morgu (2008).

Table 1: Mean Concentration of heavy metals in seawater from Qua Iboe River during Dry/Wet seasons in comparison with WHO/NESREA Standards

Sample points	Heavy metals	Dry season	Wet season	WHO (2003)	NESREA (2009)
	mg/l	Mean Conc.	Mean Conc.	mg/l	mg/l
		Dec – Feb	May – July		
P1 -P5	Pb	0.628	0.427	0.01	0.05
P1 -P5	Cu	0.072	0.049	0.01	0.05
P1 -P5	Cd	0.381	0.214	0.01	0.01
P1 -P5	Cr	0.486	0.289	0.05	0.10
P1 -P5	Ni	0.631	0.408	0.02	0.02

Higher level of heavy metals in dry season compared to wet season depends on several factors. They are; mechanism of deposition, transport of solute compounds during wet season, ion exchange of metals with sea-salt cations which reduces metals concentration in the wet season and the growth of aquatic organisms in the wet seasons unto which metals can cling (Onuoha and Morgu, 2008).

The higher level of lead (Pb) in the dry seasons might be due to evapo-crystallisation process and low precipitation signifying low dilution. Otityoju and Otityoju (2013) reported that lead in marine environment is associated with oil exploration, pipeline transportation, corrosion inhibition as well as other processes. Oladoye and Adewoyiin (2014) associated lead contamination in Ibeno to crude oil exploration while Saeed and Shaker (2008) attributed high level of lead in water to industrial and agricultural discharge as well as spill of leaded petrol from fishing boats. Other sources described by other authors include indiscriminate discharge of lead-acid battery from Ihedioha and Okoye (2013) and burning of coal and leaded gasoline from Egereonu and Ozuzu (2005).

In Ebong et. al., (2004) the concentration of lead above the permissible limit is capable of inducing abdominal pains, vomiting, drowsiness, convulsion, anaemia and malfunctioning of kidney, pancreases, brain and reproductive system. Howard et. al., (2005) confirmed that once lead is absorbed, it acts as an accumulative toxin that can deaden nerve receptors in man while Ali et. al., (2011) attributed Pb toxicity in humans to abnormal size and effect on haemoglobin content of erythrocyte, anaemia and permanent damage to the central nervous system.

The lower values of cadmium during the wet season might be due to dilution. Low levels of Cd in the wet seasons are attributed to dilution by rain water as well as run-off (Ahmed et. al., 2010). The average mean concentrations of cadmium in water sample were 0.381mg/l and 0.214mg/l for the dry and wet season respectively. These values are higher than the permissible limit proposed by WHO (2003) and NESREA (2009), Table 1.

Exposure to high levels of Cd is associated with osteoporosis and damage to kidney and loss of calcium from the bone and osteomalacia (Jarup, 2003). Oze et. al., (2005) reported that acute neurological effects of Cd toxicity manifest as nausea, abdominal cramp, bloody diarrhea, chest pain, dizziness. The “itai-itai” disease was traced to Cd contaminated rice field. They attributed Cd in Qua Iboe River to petroleum processing and effluents discharge facility at Qua Iboe River and coal, fossil fuel as well as residual deposit of metals from oil spillage.

Nickel and Chromium are essential element but could be toxic to human if found in elevated concentrations (Addo et. al., 2013). The alloying of chromites ore with metals such as iron, nickel and cobalt to form various kinds of chromium metals and ferrochromium metals and possible corrosion of these metals may be responsible for high levels of Cr in Qua Iboe River. In addition, Chromium is a component of drilling mud thinner that may be released as oil field effluent into Qua Iboe River by Exxon-Mobil. Chromium oxide is used as inorganic colour additive in soap and paint products and may be introduced as domestic waste into the marine ecosystem.

According to Udosen et. al., (2007), nickel can be introduced into the ecosystem during drilling or oil spillage. The concentrations of nickel in this study were higher in both seasons when compared to the standards. Howard et. al., (2005), stated that high levels of Ni are found in wastes from petroleum industries and chronic discharge of such wastes can result in Ni accumulation in the aquatic system. Nickel toxicity was linked to cancer of the lungs, bone and dermatitis (skin irritation) (Ebong et. al., 2004) while long term exposure to Ni can result in decreased body weight, heart and liver damage Udosen et. al., (2007). Vincoli (1985) listed several health effects due to nickel ingestion to include depression of the central nervous system (CNS) and kidney damage.

The average mean concentrations of copper in water obtained from the Qua Iboe River were 0.072mg/l and 0.049mg/l for both dry and wet seasons respectively. The value for the dry season was above the permissible limit of 0.01mg/l as recommended by (WHO, 2003) while that of the wet season was within the limit, 0.05mg/l as recommended by (NESREA, 2009). Copper is a naturally occurring metallic element that occurs in soil at an average concentration of about 50ppm. It is present in all animal and plants and is an essential nutrient for humans and animals in small amounts. The major sources of copper in marine environment include mining, smelting and refining of copper. Industries produce products from copper such as wires, pipes, sheet metals and fossil fuel combustion. Other releases of copper into the environment include agricultural use against plant diseases and treatments applied to water bodies to eliminate algae (USEPA, 1998).

Heavy metals in sediment from Qua Iboe River

The concentrations of heavy metals in sediment of Qua Iboe River in two seasons from five sampling points are presented in Table 2. The values in the dry season decreased according to the following trend: Ni > Pb > Cr > Cd > Cu while the trend for the wet season was Ni > Pb > Cr > Cd > Cu. The distribution of metals in sediments gave similar trend with that of seawater. This implies that the factors affecting the levels of heavy metals in water and sediments are similar. Similar observation was made by Bassey (2015) and Bazzi (2014).

Table 2: Mean Concentration of heavy metals in Sediment from Qua Iboe River during Dry/Wet seasons in comparison with EU and NOAA Standards

Sample points	Heavy Metals	Dry season	Wet season	European Union	NOAA
	mg/g	Mean Conc.	Mean Conc.	mg/g	mg/g
		Dec – Feb	May – July		
P1 -P5	Pb	3.552	2.121	0.300	0.035
P1 -P5	Cu	1.327	0.943	0.140	0.002
P1 -P5	Cd	2.578	1.517	0.003	0.0009
P1 -P5	Cr	2.829	1.777	0.150	0.043
P1 -P5	Ni	4.926	3.675	0.075	0.022

Although, the results indicated that the accumulation of heavy metals are predominant in sediments than seawater. This can be interpreted that sediment act as reservoir for all the contaminants and dead organic matter descending from the ecosystem above. Generally, the mean values of all the heavy metals in the dry seasons were higher than that of the wet seasons. Again, the mean concentrations of all the heavy metals in both seasons were above the maximum limit recommended by EU (2001) and NOAA (2009). The results of this study agree with the findings of Obasohan and Eguavoen (2008) which reported higher dry season mean values of heavy metals than wet season values. The observed result could be due to adsorption of metals to sediment particles because of reduced water volume usually associated with increase evaporation rate in the dry season as reported by Bassey (2015). It was reported that at low pH, metals tend to dissolve from sediments into the water column (Uwah et. al., 2013). Seasonal variation in metal concentration observed could also be as a result of slow water movement in the sediment and possible adsorption ability of trace metals by sediments (Nwadinigwe et. al., 2014).

Heavy metals in shrimps from Qua Iboe River

Table 3 revealed the concentration of heavy metals in shrimps from five sampling points of Qua Iboe River in both seasons as well as the mean concentrations of heavy metals in both seasons in comparison with International Standards. The distribution pattern of heavy metal concentration in shrimps was observed to be different from that of seawater and sediment. The metals decreased according to the order: Cu > Cr > Ni > Pb > Cd in both dry and wet seasons. The mean concentration for heavy metals during dry season were 0.008, 0.308, 0.004, 0.039 and 0.025 mg/g for Pb, Cu, Cd, Cr and Ni respectively while the values for wet seasons were 0.005, 0.196, 0.002, 0.020 and 0.017 for Pb, Cu, Cd, Cr and Ni respectively.

Table 3: Mean Concentration of heavy metals in Shrimps from Qua Iboe River during Dry/Wet seasons in comparison with International Standards

Sample points	Heavy Metals	Dry season	Wet season	International Standards	References
	mg/g	Mean Conc.	Mean Conc.	mg/g	
		Dec – Feb	May – July		
P1 -P5	Pb	0.008	0.005	0.0005	WHO/FAO (1989)
P1 -P5	Cu	0.308	0.196	0.030	WHO/FAO (1989)
P1 -P5	Cd	0.004	0.002	0.0005	WHO/FAO ((1989)
P1 -P5	Cr	0.039	0.020	0.013	USFDA (1993a)
P1 -P5	Ni	0.025	0.017	0.080	USFDA (1993b)

Copper were the most concentrated metal in shrimps of Qua Iboe River with maximum mean concentration of 0.308mg/g in dry season and 0.196mg/g in wet season. These values were similar to those reported in shrimps from Lagos lagoon system (Maria et. al., 2014). According to Rodriguez de la Rua et. al., (2005), the high concentrations of Cu are due to the capacity of shrimps to accumulate the metal in different cellular compartments, neutralizing its effects and excreting the contaminant using different physiological strategies. Increases in the accumulation of these metals have been observed with respect to exposure time and environmental concentration. The assimilation of Cu involves the formation of complexes with organic substances, which are not easily excreted (Laws, 1981). Organisms such as shrimps can maintain constant levels of Cu through ionic regulatory processes in their tissues (Scelzo, 1997).

Higher mean values of all the heavy metals (Pb, Cu, Cd, Cr and Ni) were recorded during the dry season than in the wet season. Comparing the concentration of heavy metals in this study for both seasons with maximum limit recommended by FAO/WHO (1989) and USFDA (1993a) while the mean values for all the metals were above standards exception of Ni which was below the standard set by USFDA (1993b) (Table 3).

Copper is an essential element in the human body and one of the most abundant trace metal and an essential micronutrient for almost all organisms (Duffus, 2002). Copper concentrations in crustaceans may be elevated (60 and 140 $\mu g\ g^{-1}$) compared with other groups (polychaetes and molluscs) since many crustaceans use Cu in a blood pigment (Everaarts and Nieuwenhuize, 1995). Copper is highly toxic in aquatic environments and has effects in fish, invertebrates, and amphibians, with all three groups equally sensitive to chronic toxicity (USEPA, 1993; Horne and Dunson, 1995). The metal is present in pesticides, wood preservatives, alloys fossil fuel, cooking utensils, piping and wiring. According to the Nigerian Industrial Standards for drinking water Quality (NIS, 2007), excess intake of copper can lead to gastrointestinal disorder. Other health problems associated with excess Cu uptake are anaemia, liver and kidney damage (Turnland, 1988).

In Ali et. al., (2011), long exposure to low level of Lead in aquatic organism may lead to bioaccumulation. ASTDR (2007) posited that there is no safe concentration of Lead because it replaces zinc in Heme synthesis and inhabits the function of Heme synthesizing enzymes. Akpayung et. al., (2014) highlighted that vital enzymes in Central Nervous System (CNS) are affected by substitution of Ca^{2+} by Lead, thereby affecting the development and function of enzymes involved in production and transportation of neurotransmitters. This leads to encephalopathy in children.

Cadmium contamination in shrimps may lead to slight anaemia because of competition between iron and cadmium (Alinor and Obiji, 2010; Al-Kahtani, 2009). This injures the kidneys and causes symptoms of chronic toxicity including impaired kidney function, infertility, hypertension, tumours and hepatic dysfunction cadmium (Rahman et. al., 2010).

The observed level value of Ni in this study is low when compared with the international standards. It is possible that shrimps from Qua Iboe River have efficient biotransformation mechanism for nickel or the shrimps can selectively exclude nickel from their food chain. Long exposure term discharge of oil field waste known to be high in nickel can increase the pollution level of the shrimps, since, it is a cumulative toxin. Rahman et. al. (2012) explains that low level of nickel in the environment can cause a variety of pulmonary adverse health effects such as lung inflammation, fibrosis and tumours.

Long-term exposure to low concentration of chromium may lead to kidney, liver and nerve tissue damage. Akpayung et. al., (2014) posited that low doses of chromium produces marked inhibition of glucose reabsorption due to damage to convoluted proximal tubules. Generally, exposure of shrimps to heavy metals may result in varying degrees of ion regulatory disruption. Heavy metal effluents delay embryonic development, malformation and reduced growth of mollusc and crustaceans.

SUMMARY AND CONCLUSION

Samples of seawater, sediment and shrimps obtained from Qua Iboe River during the dry and wet seasons were found to contain all the analysed heavy metals. When compared with international standards, all the metals in shrimp except Ni were above the permissible limit. For seawater and sediment, all the heavy metals were above the permissible limit. These findings suggest serious health risk to humans who use these shrimps for food and therefore recommended that Qua Iboe river should be regularly monitored by prohibiting indiscriminate discharge of domestic waste and sewage directly into the river, since water from the river is used for cultivating shrimps, fishing, swimming, irrigation and other recreational activity.

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