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RESEARCH ARTICLE

DISTRIBUTION OF TRACE ELEMENTS IN WATER, FISH AND EARTHWORM FROM WARRI RIVER IN DELTA STATE OF NIGERIA

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ABSTRACT

Water, fish and earthworm samples collected from Enerhen and Otokutu areas along the Warri River were analytically treated and analysed for trace metals using atomic absorption spectrophotometer (AAS) of Model Perkin. Elmer 311 A. A total of twelve sample points were mapped out in both Enerhen and Otokutu areas. This study was carried out for a period of six months (July – December). The results obtained showed that all the metals analysed were detected and varied from one point to another. Lowest trace metal values were obtained in water samples whereas highest mean metal values were recorded in fish samples. This is an indication that vertebrates accumulate more metals than invertebrates. Chromium, lead and iron concentrations in water exceeded the WHO limits for drinking water indicating that the water is not fit for drinking. Also, Cadmium, Copper and Lead mean values in the fish and earthworm in this study far exceeded the recommended Daily Intakes Set by Food Standards Australia New Zealand. A critical look at the results further revealed that earthworm accumulates copper levels more than the fish. This is because earthworm is a bioindicator for the availability of Copper in ecosystems. Highest mean concentrations of iron were obtained in water, fish and earthworm in that order. These elevated iron levels are attributed to activities of the Delta Steel Company located around Warri.

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INTRODUCTION

The indiscriminate disposal of the industrial as well as the domestic wastewaters has posed a perennial problems resulting in the gross water pollution to Nigerian Rivers. The coaster area of the Niger Delta Region in Nigeria is exposed to industrial and domestic waste flushed from hinterland. The contamination of fresh waters with a wide range of pollutants has become a matter of concern over times (Vutukuru, 2005; Dirilgen, 2001; Voegborlo *et al.*, 1999; Canli *et al.*, 1998). Heavy metals contamination may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organisms (Farombi *et al.*, 2007; Vosyliene and Jankaite, 2006; Ashraj, 2005). Among animal species, fishes and earthworms are the inhabitants that cannot escape from the detriment effects of these pollutants (Olaifa *et al.*, 2004; Clarkson, 1998; Dickman and Leung, 1998). Earthworms can accumulate in their tissues heavy metals in contaminated and non-contaminated environment. Fishes are widely used to evaluate the health of aquatic ecosystems because pollutants build up in the food chain and are responsible for adverse effects and the death in the aquatic

systems (Farkas *et al.*, 2002). The pollution of aquatic environment by heavy metals affects aquatic biota and Posei considerable environmental risks and concerns (Amisah *et al.*, 2009) compared with other types of aquatic pollution, heavy metal pollutants are less visible but its effects on the ecosystem and humans are intensive and very extensive due to their toxicity and their ability to accumulate in the biota (Shanmugam *et al.*, 2007; Edem *et al.*, 2008). Water contamination with organic pollutants, heavy metals and acid precipitations can be detrimental to earthworm populations. Most toxic organic water pollutants are highly toxic to earthworm. In addition to acute negative effects of some heavy metals in earthworm, sub-lethal heavy metal concentrations can cause declines in earthworm growth and reproduction (Bohlen, 2002). The metal concentration found in tissues of *Platichthys Flesus L.* and *Clupea Harengus membras L.* from the Southern Baltic Sea were varied. This research also showed that the metal concentrations in the muscles of the investigated fish species were lower than the maximum levels set by European Union (EU) legislation (Pokorska *et al.*, 2012). Concentrations of Cu, Zn, Mn, Fe, Cd, Hg, and As in muscle tissue of fish species studied from North East coast of India showed that the bioaccumulation of Fe, Zn, Cu and Mn was predominate followed by As, Hg and Cd in muscle tissue of coastal fishes

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(Kumar *et al.*, 2012). Bioaccumulation is an important factor in the assessment of environmental hazard (Heng *et al.*, 2004). Essential and non-essential trace elements are known to be highly accumulated by invertebrates, in particular by a variety of molluse and annelids species (Eze Monys *et al.*, 2006). The toxic effects of heavy metals have been reviewed, including bioaccumulation [Wagar (2006) Aucoin *et al.* (1999)].

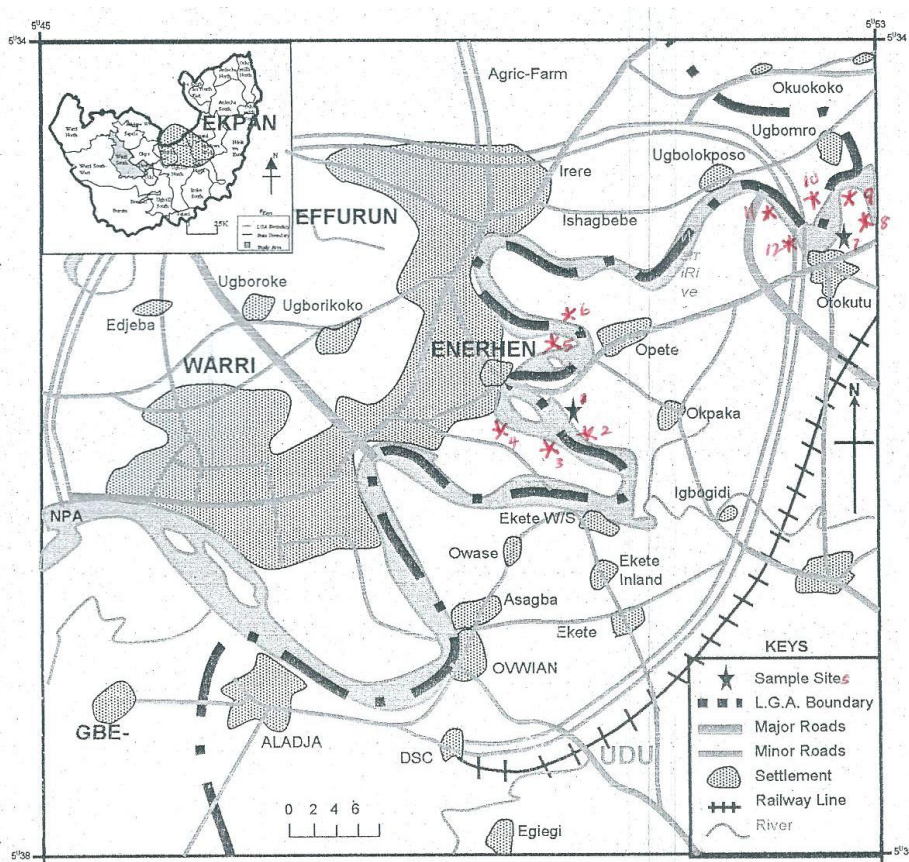
The base of the marine food chain consist of plankton life abundant in the upper 3mm of oceanwater. Earthworm and the young of certain fish and shellfish also reside in the upper few millimeters of water in the early stages of their life (Botkin and Keller, 1998). Unfortunately, the upper few millimeters of the ocean also tend to concentrate pollutants such as toxic chemicals and heavy metals. However, there is fear that disproportionate pollution of this few 3mm will have especially serious effects on marine organisms. Dumping wastes into rivers contribute to the larger problem of river pollution which can seriously damage the marine environment and cause health hazards to aquatic organisms. The problem of water pollution due to toxic metals has begun to cause concern now in most metropolitan cities (Malik *et al.*, 2010; Abdel-Baki *et al.*, 2011). The importance of environmental quality in Otokutu and Enerhen areas in Warri town has recently attached a great deal of interest hence it became necessary for this study, since fishes and earthworms are used as indicators of heavy metals contamination in the aquatic ecosystems. The objectives of this study therefore are: to determine the trace metals content in fishes and earthworm from Warri River and to determine the pollution status of Warri River, if any.

MATERIALS AND METHODS

Description of the study area

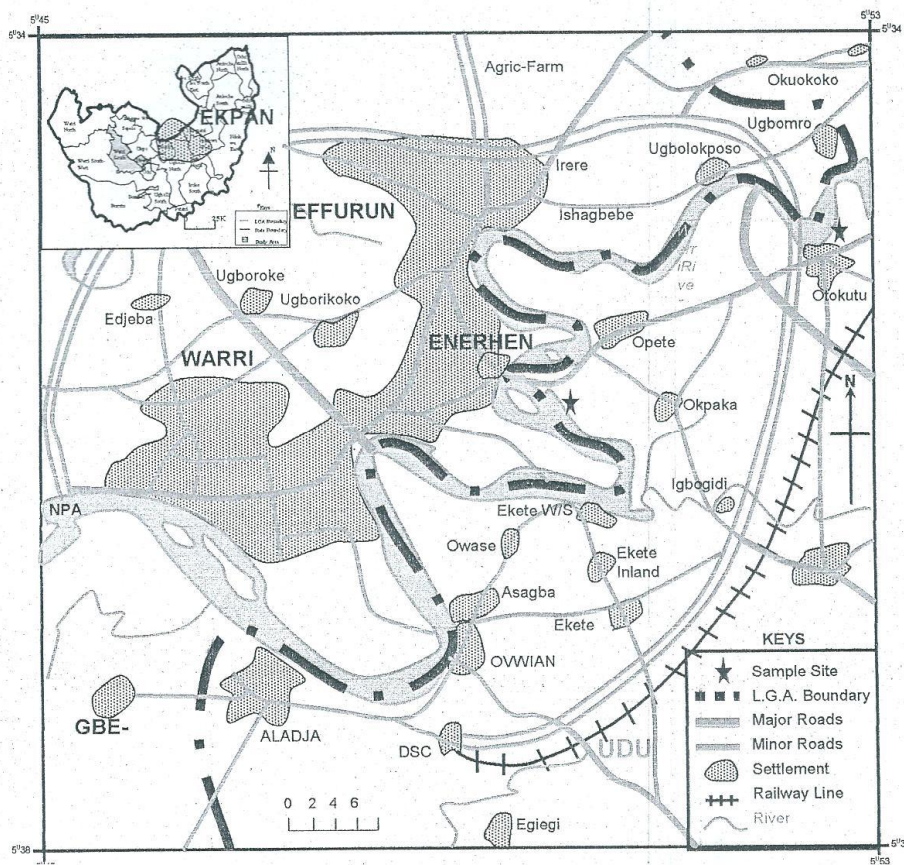
Warri metropolis is located between Latitude 5°31' N and 5°35' N, and Longitude 5°29' E and 5°48' E. The study area is situated within Niger Delta Region of Nigeria and bounded to the North by Okpe and Sapele Local Government Areas; to the South by Warri South West and the Atlantic Ocean; to the East by Ughelli South and to the West by Warri North Local Government Area. The expansion of Warri in the past two decades has been remarkable from a small riverine settlement. Warri has grown to cover the surrounding towns of Effurun, Ekpan, Enerhen, Edjeba, Ogunu, Jakpa, Ovwian – Aladja and Udu road respectively. The land mass of Warri is now over 100 square kilometres (Efe, 2002).

The terrain is flat having an elevation of 6.10m above sea level and located at the shores of Warri River, and Ovwian River. The area is characterized by hydromorphic soils, which is a mixture of coarse alluvial and colluvial deposit. The soils are poorly drained and accumulated with water because it is nearer to the Atlantic Coast, having a high water table close to the surface. The area is also characterized by tropical equatorial climate with mean annual temperature of 27.44°C, average relative humidity of about 70% to 80% and annual rainfall amount 3302.52mm (Efe, 2002). Warri metropolis is one of the rapidly growing cities in Nigeria.



Source: Modified after Ministry of Lands, Survey and Urban Development Asaba

Fig. 1. Map of Warri Metropolis showing sample sites



Source: Modified after Ministry of Lands, Survey and Urban Development Asaba

Fig. 1. Map of Warri Metropolis showing sample sites

Sample Collection

Water, fish and earthworm samples were collected in two sections named Otokutu and Enerhen along the Warri River. Six sample points were created in each of the sections. A total of twelve sample points were selected for this study for the period of six months (i.e. July – December, 2013).

Catfish (*Synodontis nigrita*), earthworm (*Libydrilus violaceons*) and water samples were collected from six sample points in each of the two sections along the Warri River. The fish and earthworm samples collected were labeled, ice preserved and transported to the main laboratory. The water samples were transferred into polythen bottles rinsed with HNO_3 for several times and later added 5% HNO_3 and were stored at 4°C in the refrigerator (Nwajei *et al.*, 2012; Kumar *et al.*, 2010). The fish and earthworm were caught and processed. Thereafter, they were thoroughly washed to remove all the adhered soil particles then placed onto glass petri dishes and placed into hot air oven at 80°C until reaching a constant weight. The dried fish and earthworm (whole body) were grounded into powder using porcelain mortar and pestles. Thereafter, they passed through 2mm sieve (Rakesh *et al.*, 2013).

Digestion of Samples

One gramme of each sample (fish and earthworm) was weighed and then digested in acid mixture with 20ml HNO_3

and 5ml HClO_4 . The solutions were constantly stirred while on the hot plate and transferred into the fumehood and left overnight. The next day, the solutions were cooled and filtered. The filtrates were made up to 100ml in volumetric flask using deionized water. The solutions were stored in a refrigerator prior to metal analysis using atomic absorption spectrophotometry.

Quality Control/Assurance

In order to ensure the accuracy and reliability of the results obtained, and all reagents used for the preparation of standard solutions and analysis were of analytical grades (BDH) All glassware and plastic containers were acid-washed. Bulk Scientific Standard Solutions were used for calibrations. Procedural blank samples were subjected to similar extraction method using the same amount of reagents. The analysis were done in triplicates.

Statistical Analysis

Metal concentrations in water, earthworm and fish tissue samples were evaluated statistically using analysis of variance (ANOVA) technique.

RESULTS AND DISCUSSION

The concentrations for all elements determined in water, earthworm and fish in Warri River were all above the detention limits.

Table 1. Mean \pm S.D of Metal Concentrations (mg/l) in Warri River at Otokutu and Enerhen Areas

Metals in mg/l	Sample Point 01	Sample Point 02	Sample Point 03	Sample Point 04	Sample Point 05	Sample Point 06	Sample Point 07	Sample Point 08	Sample Point 09	Sample Point 10	Sample Point 11	Sample Point 12
Cr	0.04 \pm 0.00	0.08 \pm 0.02	0.04 \pm 0.00	0.03 \pm 0.00	0.40 \pm 0.10	0.80 \pm 0.10	0.04 \pm 0.00	0.04 \pm 0.00	0.04 \pm 0.00	0.40 \pm 0.10	0.60 \pm 0.20	1.00 \pm 0.00
Cu	0.60 \pm 0.10	1.10 \pm 0.03	0.60 \pm 0.10	0.90 \pm 0.20	1.00 \pm 0.00	1.20 \pm 0.10	0.40 \pm 0.10	0.80 \pm 0.20	0.40 \pm 0.02	1.00 \pm 0.10	1.30 \pm 0.10	1.00 \pm 0.20
Ba	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.00	0.03 \pm 0.01	0.02 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.04 \pm 0.00	0.06 \pm 0.01	0.01 \pm 0.00
Pb	0.08 \pm 0.00	0.10 \pm 0.00	0.20 \pm 0.00	0.8 \pm 0.20	0.80 \pm 0.20	0.80 \pm 0.20	0.08 \pm 0.00	0.10 \pm 0.00	0.40 \pm 0.00	0.60 \pm 0.00	1.00 \pm 0.00	0.40 \pm 0.10
Cd	0.01 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.10 \pm 0.00	0.10 \pm 0.00	0.40 \pm 0.10	0.01 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.08 \pm 0.00	0.10 \pm 0.02	0.30 \pm 0.00
Fe	1.20 \pm 0.20	1.00 \pm 0.00	1.10 \pm 0.30	1.30 \pm 0.20	1.10 \pm 0.30	1.40 \pm 0.20	1.70 \pm 0.30	1.00 \pm 0.10	1.30 \pm 0.40	1.90 \pm 0.10	1.70 \pm 0.20	1.30 \pm 0.20

Table 2. Mean \pm S.D of Metal Concentrations (mg/kg dry wt) in Earthworms from Otokutu and Enerhen Areas along the Warri River

Metals in mg/l	Sample Point 01	Sample Point 02	Sample Point 03	Sample Point 04	Sample Point 05	Sample Point 06	Sample Point 07	Sample Point 08	Sample Point 09	Sample Point 10	Sample Point 11	Sample Point 12
Cr	0.90 \pm 0.30	0.70 \pm 0.20	1.30 \pm 0.40	1.00 \pm 0.30	0.80 \pm 0.10	1.00 \pm 0.20	1.10 \pm 0.20	1.80 \pm 0.20	1.00 \pm 0.20	1.00 \pm 0.10	1.00 \pm 0.30	1.40 \pm 0.20
Cu	8.10 \pm 0.40	4.00 \pm 0.50	1.90 \pm 0.30	1.70 \pm 0.40	1.40 \pm 0.20	1.80 \pm 0.30	6.60 \pm 0.40	4.80 \pm 0.40	2.30 \pm 0.70	1.90 \pm 0.30	1.40 \pm 0.20	2.10 \pm 0.40
Ba	0.10 \pm 0.00	0.20 \pm 0.00	0.10 \pm 0.00	0.03 \pm 0.00	0.01 \pm 0.00	0.03 \pm 0.00	0.30 \pm 0.00	0.10 \pm 0.00	0.10 \pm 0.00	0.04 \pm 0.00	0.02 \pm 0.00	0.04 \pm 0.00
Pb	1.30 \pm 0.20	1.00 \pm 0.00	0.60 \pm 0.10	0.40 \pm 0.00	0.30 \pm 0.00	0.80 \pm 0.10	1.00 \pm 0.20	0.60 \pm 0.10	0.80 \pm 0.10	0.30 \pm 0.00	0.40 \pm 0.10	0.40 \pm 0.00
Cd	1.00 \pm 0.10	1.00 \pm 0.00	0.60 \pm 0.10	0.30 \pm 0.00	0.40 \pm 0.10	0.70 \pm 0.20	1.20 \pm 0.40	0.60 \pm 0.10	0.80 \pm 0.20	0.40 \pm 0.00	0.60 \pm 0.10	1.00 \pm 0.00
Fe	1.90 \pm 0.40	2.20 \pm 0.20	2.70 \pm 0.90	1.70 \pm 0.20	1.70 \pm 0.30	1.40 \pm 0.10	3.30 \pm 0.90	2.80 \pm 0.70	2.10 \pm 0.40	1.40 \pm 0.40	1.30 \pm 0.20	1.70 \pm 0.20

Table 3. Mean \pm SD of Metal Concentrations (mg/kg dry wt) in fish from Otokutu and Enerhen Areas along the Warri River

Metals in mg/l	Sample Point 01	Sample Point 02	Sample Point 03	Sample Point 04	Sample Point 05	Sample Point 06	Sample Point 07	Sample Point 08	Sample Point 09	Sample Point 10	Sample Point 11	Sample Point 12
Cr	0.40 \pm 0.01	0.040 \pm 0.00	0.04 \pm 0.00	1.04 \pm 0.01	0.07 \pm 0.01	0.30 \pm 0.02	0.06 \pm 0.00	1.10 \pm 0.00	0.04 \pm 0.00	0.08 \pm 0.01	0.10 \pm 0.01	0.40 \pm 0.10
Cu	1.20 \pm 0.40	1.20 \pm 0.40	1.70 \pm 0.70	1.00 \pm 0.20	1.10 \pm 0.10	1.30 \pm 0.20	1.80 \pm 0.60	1.10 \pm 0.30	1.00 \pm 0.10	1.10 \pm 0.10	1.00 \pm 0.20	1.40 \pm 0.30
Ba	0.03 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.03 \pm 0.00	0.02 \pm 0.00	0.30 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.03 \pm 0.00	0.05 \pm 0.01	0.02 \pm 0.00
Pb	0.10 \pm 0.00	0.10 \pm 0.00	0.10 \pm 0.00	0.10 \pm 0.00	0.10 \pm 0.20	0.20 \pm 0.02	0.20 \pm 0.01	0.10 \pm 0.00	0.10 \pm 0.00	0.10 \pm 0.00	0.10 \pm 0.00	0.30 \pm 0.06
Cd	0.04 \pm 0.01	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.08 \pm 0.00	0.06 \pm 0.01	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Fe	3.30 \pm 0.80	2.40 \pm 0.60	2.00 \pm 0.80	1.20 \pm 0.20	1.40 \pm 0.10	1.60 \pm 0.30	2.80 \pm 0.40	2.20 \pm 0.30	1.90 \pm 0.50	1.60 \pm 0.20	1.80 \pm 0.30	1.40 \pm 0.30

* Mean \pm SD = Mean and Standard Deviation

Secondly, metal concentrations varied across the sampling sites. The bioaccumulation of the monitored metal also varied between earthworms and fishes. The differences in bioaccumulation in earthworms and fishes revealed that the invertebrates' rate of metal uptake was higher than those of the vertebrates. Lowest metal concentrations were obtained in the water samples across the sample sites; this was followed by the fish and the earthworm respectively. Warri metropolis is known to be highly industrialized, hence it is expected that Warri River could trap all the pollution loads which find ways into it. This has reflected in the concentrations of metals in water from the Enerhen and Otokutu areas along the Warri River. The concentrations of Ba and Cd in water in this study were within the WHO limits whereas metals such as Cr, Pb and Fe exceeded the maximum allowable concentrations. On the other hand, Cu concentrations were lower than the WHO standard for drinking water.

Chromium (VI) can cause many health effects. Tobacco smokers have higher possibility of dislouse to Chromium. The Chromium levels in this study are considered elevated. Fish being at a higher level of the food chain accumulate large quantities of metals and the accumulation depends upon the intake and elimination from the body (Karadede *et al.*, 2004). Some fish have poisonous effect of Chromium as echoed in the blood changes such as anemia and other diseases. The elevated content of Chromium in this study is attributed to anthropogenic activities when natural water is being contaminated by this metal. The accumulation of Chromium in this study is in this order: Water < fish < earthworm.

Copper contents in fish, earthworm and water varied, the fish accumulated highest concentrations than those of the earthworm whereas least copper contents were obtained in water. The bioaccumulation levels are arranged in this order water < earthworm < fish respectively. However, there were no significant variations in copper concentrations in the samples obtained from Enerhen and Otokutu areas. Copper level in this study is not dangerous to human health, because it is an essential mineral needed in human body. The levels of Copper obtained here could be used for producing and storing iron in aquatic life. This study further revealed that vertebrates accumulate copper more than invertebrates in Nigerian rivers. Barium concentrations in water, and earthworm were very low and insignificant to cause threat to aquatic life. The low level of barium in this study was unexpected because barium compounds are used by the oil and gas industries to make drilling mud. Warri, where this study was carried out is one of the major oil locations in the Niger Delta Region of Nigeria. Barium compounds that are released during industrial processes could dissolve easily in water and get into the rivers for vertebrates and invertebrates absorption.

The concentrations of lead in water in this study were elevated and considered higher than the WHO limits for drinking water. Lead contents in vertebrates (fish) were higher than those obtained in the water and earthworm samples from both Enerhen and Otokutu areas of the Warri River. This study has revealed that vertebrate organisms accumulate higher Lead content than the invertebrate organisms. The concentrations of Lead in water and fish in this study exceeded the levels

reported by Abdel-Baki *et al.* (2011). The average Lead contents in this study were higher than 0.01 mg/kg Lead, Recommended Daily Intakes (RDI) set by Food Standards Australia New Zealand (FSANZ). Some types of industrial and municipal facilities and use of an additive in paints, gasoline, Leaded pipes and ceramics must have contributed to the presence of Lead in Warri River through run-off. Children tend to absorb a higher fraction of ingested Lead from the gastrointestinal tract than adults. Lead is able to be absorbed far greater than its ability to be metabolized or be excreted. Highest Cadmium levels were obtained in water in station 06 (0.40mg/l) and station 12 (0.30mg/l) whereas the average range of Cadmium in other stations was 0.01 to 0.10 mg/l. These levels are slightly higher than the WHO (2005) limits for drinking water. The average range of Cadmium in earthworm was 0.01 to 0.08 mg/kg whereas the average of Cadmium in fish was 0.30 to 1.20mg/kg, indicating that organism with backbones (fish) accumulate more Cadmium than those without backbone (earthworm). Cadmium concentrations in water, fish and earthworm were higher than the recommended daily intakes of 0.005mg/kg Cadmium set by Food Standards Australia New Zealand. (FSANZ) (FSANZ, 2013).

Burning of fossil fuels and municipal waste through runoff and precipitation into the Warri River must be responsible for the availability of Cadmium poison. This study revealed that metals accumulate in tissue and body of fish in higher concentrations than in Water. Iron contents in water from Enerhen and Otokutu areas of the Warri River ranged from 1.00 to 1.40mg/l for Enerhen and 1.00 to 1.70mg/l for Otokutu. The concentrations of iron in water from areas in Warri River exceeded 0.3mg/l set by the WHO (2005) standard for drinking water. Iron contents in the fish and earthworm were higher than those levels in Water. The average accumulated levels of iron in fish ranged from 1.40 to 2.70mg/kg for Enerhen area; and 1.30 to 3.30mg/kg for Otokutu area whereas the average iron concentrations in earthworm ranged from 1.20 to 3.30mg/kg for Enerhen area and 1.40 to 2.80mg/kg for Otokutu area. However, there was significant difference in the rate of uptake of iron by fish and earthworm. The high contents of iron in this study were attributed to activities of the Delta Steel Company (DSC) located in Warri and anthropogenic wastes channeled through the gutters into the Warri River. High levels of iron in fish could have negative effects on fish consumers especially when they exceed the total body burden.

Conclusion

Water, fish and earthworms samples obtained in Enerhen and Otokutu areas in Warri River assayed analytically revealed that metal concentrations were all detected and values vary among the twelve sample stations. Highest metal concentrations were found in the fish; followed by the earthworm and lastly the water sample. A look at metal concentrations in fish and earthworm showed that fish has higher uptake and bioaccumulation of metals when compared with earthworm. Chromium, Lead and iron concentrations in water exceeded the WHO limits for drinking water, indicating that the water is not fit for drinking. Cadmium, Copper and Lead concentrations in fish and earthworm in this study exceeded the Recommended Daily Intakes set by Food Standards Australia New Zealand. The metal concentrations in fish and earthworm in this study

could be used as an indicator to monitor metals in vertebrates and invertebrates in Nigerian rivers. Oil exploration activities, Delta Steel Company and anthropogenic wastes could account for levels of metals in Warri River.

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