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Temporal Survey of Heavy Metal Loads in Surface Water, Sediments and Shrimps from Iko River Estuary, Eastern Obolo L.G.A, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. This work was conceived by author EPU. Author NDE was responsible for the statistical analysis and writing of the manuscript. All authors were jointly involved in the design of the work and the laboratory activities. All authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Aims: *This work aimed at providing pieces of information on the trend and levels of heavy metals in shrimp, surface water and sediment from Iko river estuary, Eastern Obolo, South-South Nigeria.*
Study Design: The study area was demarcated into three stations for sampling. The sampling stations were subjectively categorized.
Place and Duration of Study: The study which was carried out in *Iko river estuary, Eastern* Obolo, South-South Nigeria lasted for 12 months.
Methodology: *Samples were collected once a month for 12 months in a consecutive manner and analyzed using standard methods.*
Results: When compared to water and shrimps, sediments contained the highest concentration of heavy metals during the study period. Contrarily, water had the highest concentration (1.50 Mg/L) of Cd, compared to 0.85 Mg/Kg in sediment and 0.27 Mg/Kg in shrimps. Levels of Lead (Pb) in the

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study samples followed a similar trend like that of Cd. Zinc also followed a contrary pattern with shrimps having the highest concentration (65.35 Mg/L). Of all the metals studied, iron (Fe) was found to be the most abundant heavy metal in Iko River Estuary. Although levels of Fe were generally high in all the samples studied, concentration in sediment (113.99 Mg/Kg) far outweighed the concentrations in shrimps (227.11 Mg/Kg) and in water (184.35 Mg/L). These levels of heavy metals determined in the water, sediment and shrimps showed variations during the wet and dry seasons.

Conclusion: The values were higher than the recommended limits. It can therefore be concluded that Iko River Estuary was always laden with heavy metals notwithstanding the season of the year. Accumulation of these metals in shrimps also indicates that sea foods from this river may not be suitable for consumption.

Keywords: Heavy metals; pollution; water; sediments; shrimps; Iko estuary.

1. INTRODUCTION

The increasing human population commonly associated to areas of oil exploration activities and the consequent increase in the levels of anthropogenic pollutants have caused serious water quality deterioration problems world-wide (Islam and Tanaka, 2004). Environmental contamination and pollution by heavy metals is a threat to the environment; and is of serious concern [1]. These chemical pollutants can be accumulated in three basic reservoirs: water, sediment and biota [2]. The distribution of metals in the environment is governed by the properties of the metal and influences of environment [3]. Although, some individuals are primarily exposed to these contaminants in the workplace, for most people the main route of exposure to these toxic elements is through diet (food and water).The contamination chain of heavy metals almost always follow a cyclic order; industry, atmosphere, soil, water, food and human. Some metals have critically important physiological and biological functions in biological systems; and either their deficiency or excess can lead to disturbance of metabolism and therefore to various disease [4]. Lead is used to produce batteries, ammunition, roofing sheets and as screens for x-rays and radioactive emissions. Food is one of the major sources of lead exposure. The others are air (mainly lead dust originating from petrol) and drinking water. Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death. In pregnant women, it may cause miscarriages and in men damage to organs responsible for sperm production [5]. The WHO provisional guideline of 0.01 Mg/L has been adopted as the standard for drinking water [6]. Several reports [7,8], (Castro-Gonzalez and Mendez – Armenta, 2008) have shown that cadmium is a very toxic metal but has many uses including batteries, pigments, metal coatings and plastics. It is used extensively in electroplating. People are exposed to cadmium by consumption of plant and animal – based foods. Sea food such as mollusks and crustaceans can be also a source of cadmium. Smokers get exposed to significantly higher cadmium levels than non-smokers during smoking. Cadmium accumulated in the human body affects the liver, kidney, lungs, bones, placenta, brain and the central nervous system negatively (Castro-Gonzalez and Mendez-Armenta, 2008). Other effects are reproductive and development toxicity, hepatic, hematological and immunological disorders [9,10]. The EPA maximum contaminant level for cadmium in drinking water is 0.005 Mg/L whereas the WHO adopted the provisional guideline of 0.003 Mg/L [6]. Chromium is used in metal alloys such as stainless steel; protective coatings on metals (electroplating); magnetic tapes, cement, composition of floor covering andother materials. Fertilizers also usually contain significant contents of chromium [11]. Breathing of high levels of chromium can cause irritation to the lining of the nose; nose ulcers; runny nose; and breathing problems such as asthma, cough, and shortness of breath or wheezing. Skin contact can cause skin ulcers. Allergic reactions consisting of severe redness and swelling of the skin have been noted [10]. Long- term exposure can harm the cause damage to liver, kidneyskidney, circulatory system, and nerves,nerve tissues as well as cause skin irritation. EPA regulatory limit is 0.1ppm in drinking water [5]. With the increasing population in most lucrative parts of Akwa Ibom State and subsequent location of oil industries in the area, pollution of the environment by the different activities in the locality has become a serious problem in the State. A temporo-spatial assessment of the heavy metal distribution in surface water, biota and sediments from the river estuary becomes quite expedient. This work was therefore designed to achieve this objective.

2. MATERIALS AND METHODS

2.1 The Study Area

Iko River Estuary in Eastern Obolo Local Government Area of AkwaIbom State is located within the Niger Delta area of Nigeria between latitude 7°3′ N and 7°45′N and longitude 7°30′ E and 7° 40′ E (Fig. 1). The Iko River estuary has semi-diurnal tides and a shallow depth ranging from 1 to 7 m at flood and ebb tide; and is more than 20 km long with an average width of about 16 m [12]. Iko River takes its course from Qua Iboe River catchments and drains directly into the Atlantic Ocean at the Bight of Bonny [12,13]. The estuary has adjoining creeks, channels and tributaries which is significant in the provision of suitable breeding site for the diverse aquatic resources that abound in the area, good fishing ground for artisanal fisherman as well as petroleum exploration and production activities. Part of the river also drains into Imo River Estuary, which opens into the Atlantic Ocean at the Bight of Bonny [13]. The area is characterized by a humid tropical climate with rainfall reaching about 3,000 mm per annum [13]. The area has distinct wet and dry seasons. The wet season begins in April and last till October, while the dry season begins in November till March. The estuary constitutes a major inlet to the land and is often utilized by inhabitants as the main transport route. It is a multi-use resource with fishery as the most dominant. The estuary also serves as the receiving water body for domestic and industrial wastes [14].

2.2 Study Design

The study area was demarcated into three stations for sampling. The sampling stations designated as Station 1(ST 1) - Utapete, located near an abandoned well-head; Station 2 (ST 2) - Iko, where dredging activities took place; and Station 3 (ST 3) - Edonwhii, which opens into the Atlantic Ocean, were subjectively categorized as upstream, midstream and downstream respectively. Sampling was carried out monthly for a year covering peak period of wet and dry seasons. Water samples for physicochemical analysis were collected concurrently at each station.

2.3 Collection of Samples

Surface water samples from each Station were collected with 1 litre water sampler into a thoroughly rinsed 1 litre glass bottle (amber bottle) and stored for DO and BOD5 analysis. For other physicochemical parameters, 2 litres capacity Polyethelene containers were used for

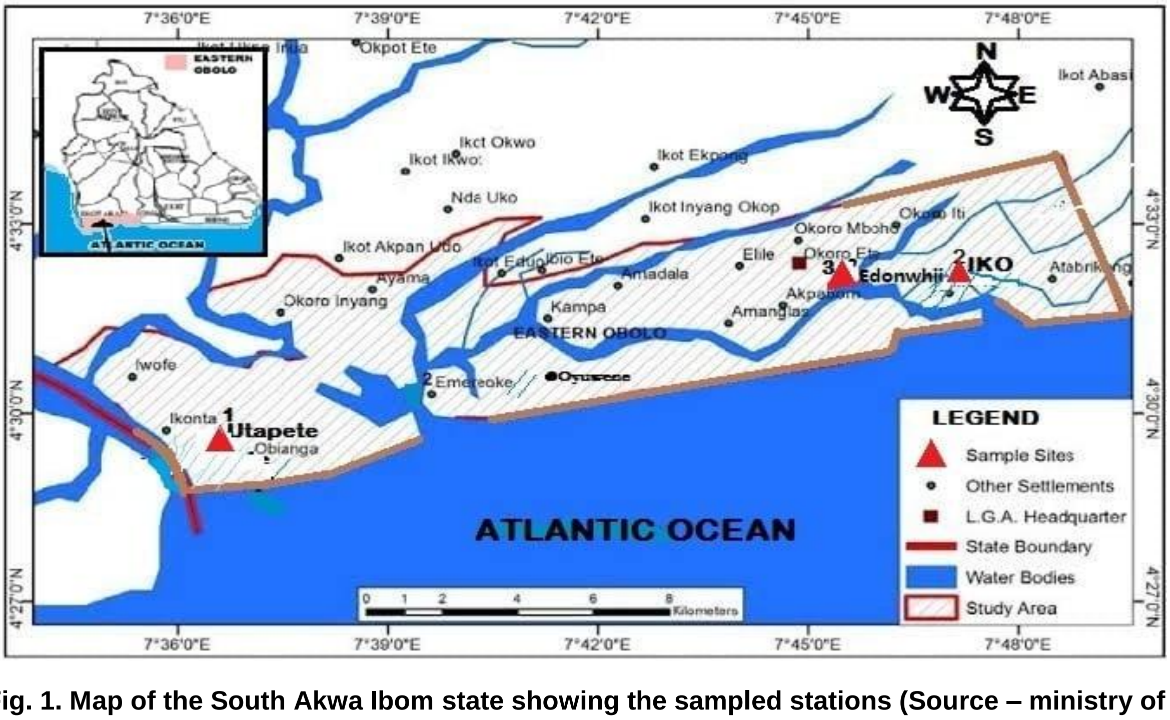

Fig. 1. Map of the South Akwa Ibom state showing the sampled stations (Source – ministry of lands and town planning, Akwa Ibom state)

water sample collection.Samples were transported with ice-chest container to the Zoology laboratory, University of Uyo for further analysis of other parameters. Each sample bottles were properly labelled, describing the different stations, date and time of sampling.

Sediment samples were collected by scooping (using a short core sampler, Kajak corer‟ model 13.030) the top 1-5 cm of intertidal mudflats; mixed together for homogeneity and the subsamples transferred into polytene bags.

Biological specimens were collected concurrently at each station.

2.4 Heavy Metal Analysis

Analysis of samples for heavy metals was done using an Atomic Absorption Spectrophotometer [15]. Samples were first digested. For water sample, 200 mL of a well-mixed/filtered sample was measured into a clean beaker and 3 Ml of concentrated HNO_3 was added. The beaker was heated on a boiling water bath to concentrate the solution to about 15 Ml. The solution was allowed to cool and filtered into a 50 ml volumetric flask. The solution was made up to the mark with deionised water and transferred into a polyethylene sample bottle for instrumental analysis. All sediments samples were oven dried at 80 - 100°C, gently crushed and sieved to collect the < 63 μ grain size. Accurately weighed (1.0 g) samples of sieved sediments were treated with 10 ml of 0.25 M HNO_3, heated to dryness and thereafter 10 ml of 0.25 M HNO_3 and 3.0 Ml of $HClO_4$ added. Sample solutions were obtained by leaching residues with 4.0 Ml of HCL and thereafter filtered and diluted with distilled water to 100 Ml mark (Binning and Baird, 2001).

Blank digestion was prepared following the same procedure with deionised water but without the sample.The Atomic Absorption Spectrophotometer was calibrated with all the standard stock solutions of the metals determined. The working standard solutions were prepared by diluting a certain volume of the stock solution of 1000 Mg/L concentration of each metal to an appropriate concentration in a volumetric flask. The working standards were aspirated appropriately into the flame and the standard absorbance determined. A standard curve of absorbance versus concentration (in MgL^{-1}) was plotted automatically by the instrument which was displayed on the readout device. The calibration curve was plotted manually and compared with the plot that was displayed on the readout device. The precision of the instrument was checked from time to time by re-running one or two of the standard solutions used for calibration.The concentrations of Cd, Cr, Pb Cu, Zn, Ni, Fe, Mn and Vanadium were determined, using a flame atomic absorption spectrophotometer (UNICAM 939/59). The operating conditions equipped with the appropriate hollow cathode lamps, air-acetylene flame and resonance wavelength of the metals. The samples were aspirated into the instrument successively and the absorbance and concentration of the sample (in ppm) was displayed on the screen. The wavelengths used in this analysis were: 228.8 nm for Cd, 283.3.0 nm for Pb, 357.9 nm for Cr, 324.8 nm for Cu, 213.9 nm for Zn, 232.0 nm for Ni, 248.3 nm for Fe, 279.5nm for Mn and 318.4 nm for V. Calibration standards were prepared from standard stock solutions of each of the metals.

2.5 Calculation

Metal concentration in the sample solution was calculated using the formula adapted by Wodaje and Alemayehu [16]:

$$\text{Metal concentration (mgL)} = A \times B/Q$$

Where,

A = conc. of element (instrument reading) in diluted solution (mgL^{-1})
B = final volume of diluted solution (mL)
Q = initial volume of aliquot taken for dilution (mL)

2.6 Data Analysis

All data were analysed using Statistical Package for Social Sciences (SPSS) software, version 21.Percentage analysis, ANOVA and Fisher's exact tests were used as appropriate.

3. RESULTS

3.1 Trends in Heavy Metal Levels in Water, Sediment and Shrimps from Iko River Estuary

The result in Fig. 2(a-i) gives information on the trend and levels of heavy metals in shrimp, water and sediment of the study area. When compared to water and shrimps, sediments contained the highest concentration of heavy metals during the study period.

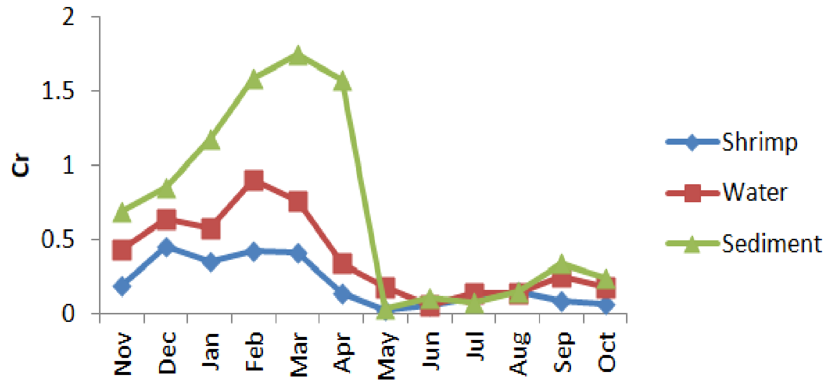

Fig. 2a. Monthly variation of Cr in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

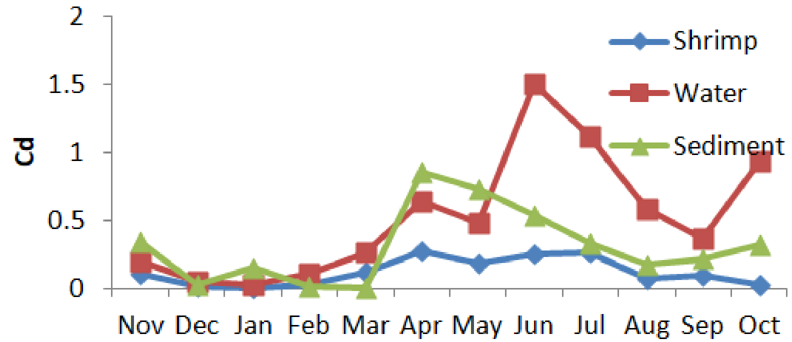

Fig. 2b. Monthly variation of Cd in in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

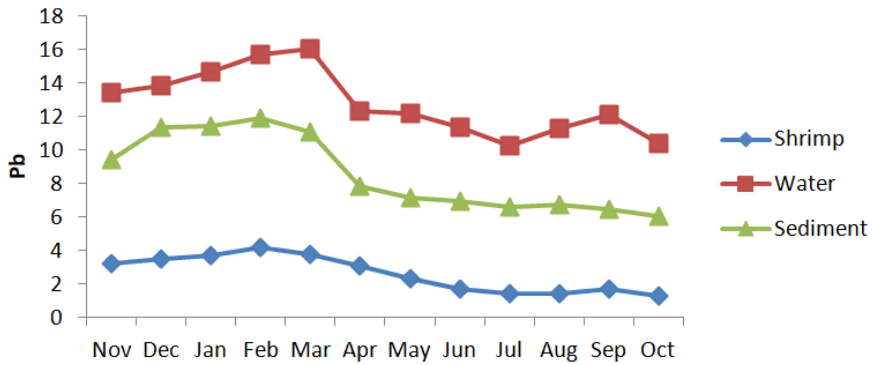

Fig. 2c. Monthly variation of Pb in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

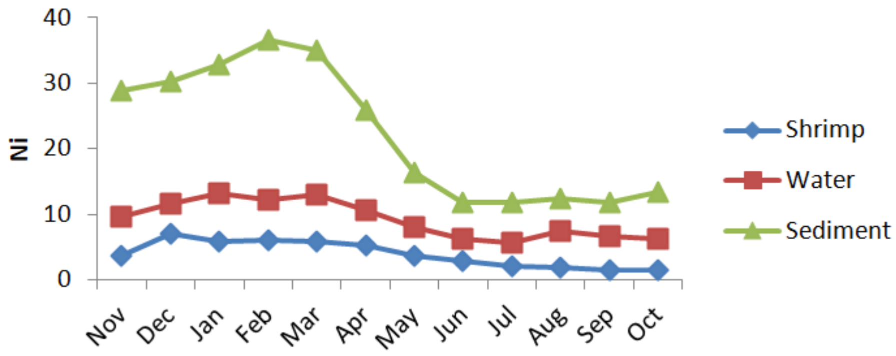

Fig. 2d. Monthly variation of Ni in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

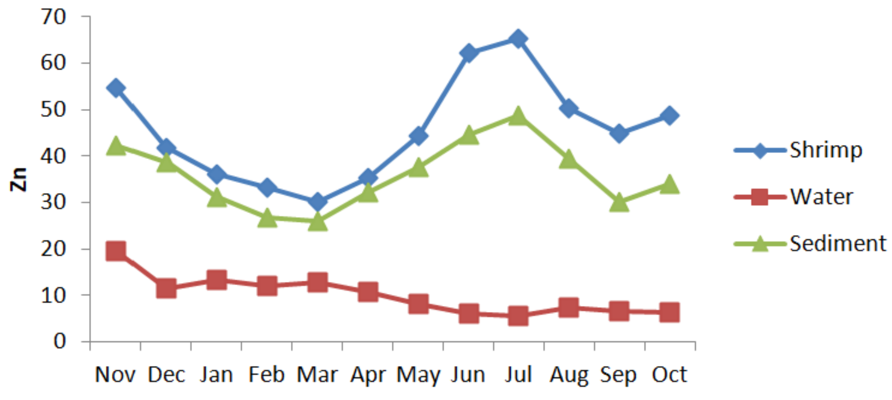

Fig. 2e. Monthly variation of Zn in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

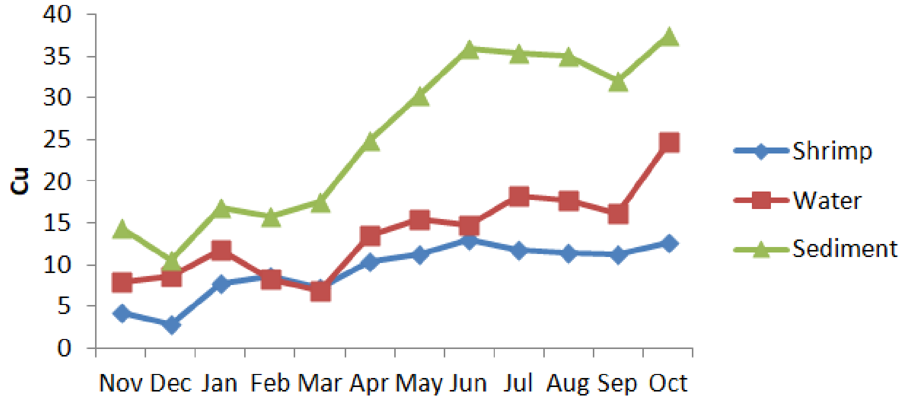

Fig. 2f. Monthly variation of Cu in in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

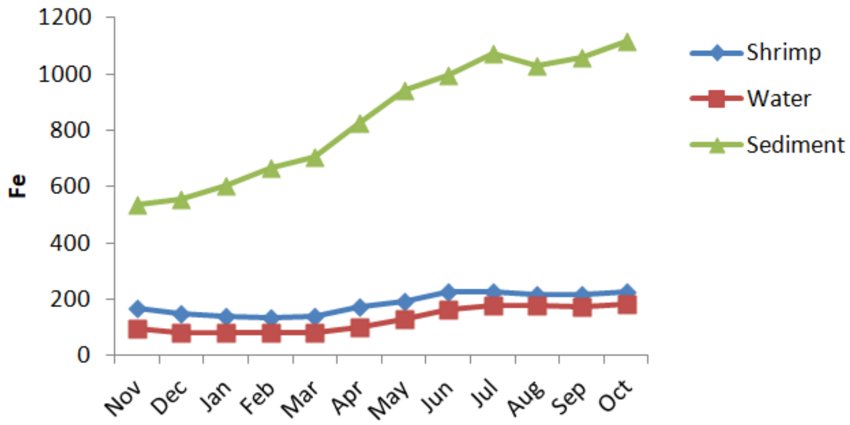

Fig. 2g. Monthly variation of Fe in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

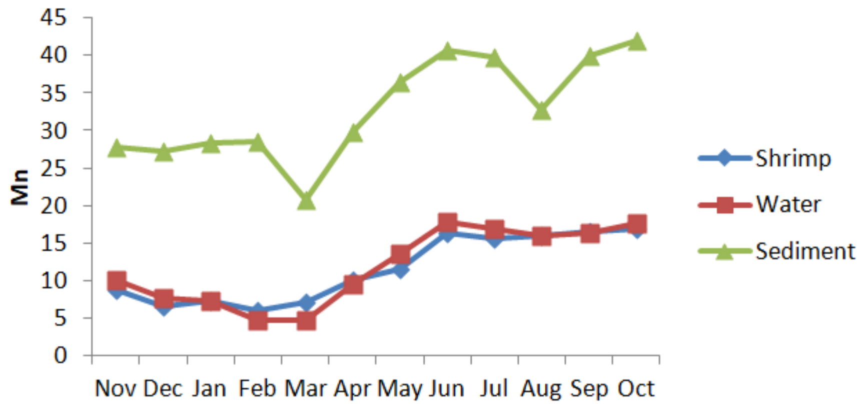

Fig. 2h. Monthly variation of Mn in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

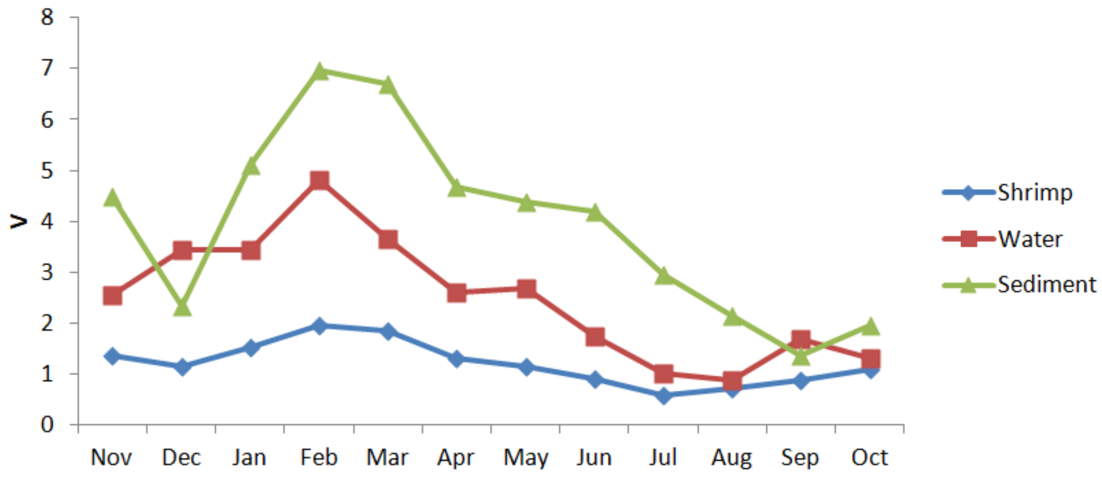

Fig. 2i. Monthly variation of V in Shrimp (Mg/Kg), water (Mg/L) and sediment (Mg/Kg)

Table 1. Mean seasonal concentration of heavy metals in water, sediment and Shrimps at different seasons

		Cr	Cd	Pb	Ni	Zn	Cu	Fe	Mn	V
Water (Mg/L)	Dry Season	0.66±0.24	0.12±0.11	14.73±3.61	11.87±3.22	36.41±15.87	8.68±2.42	83.40±12.03	6.90±2.32	3.57±1.05
	Wet Season	0.18±0.20	0.37±0.22	11.42±2.17	7.23±2.74	49.46±13.64	17.25±5.28	158.28±36.50	15.42±3.93	1.70±0.79
Sediment (Mg/Kg)	Dry Season	1.21±0.46	0.14±0.13	11.05±2.38	32.70±4.34	33.02±8.59	15.04±3.17	613.79±75.88	26.57±4.51	5.14±2.00
	Wet Season	0.22±0.20	0.45±0.26	6.83±1.71	14.72±6.24	38.10±7.65	33.01±5.80	1005.56±167.66	37.37±5.24	3.10±1.39
Shrimps (Mg/Kg)	Dry Season	0.36±0.12	0.04±0.05	3.68±0.56	5.72±2.00	39.22±11.37	6.10±2.96	146.46±26.54	7.17±2.10	1.56±0.33
	Wet Season	0.09±0.60	0.18±0.08	1.86±0.73	2.66±1.49	50.19±13.45	11.66±2.67	211.21±34.06	14.71±4.70	0.95± 0.28

The highest concentration of Cr (1.75 Mg/Kg) was obtained in the sediments samples in March, followed by 0.90 Mg/L in water and 0.42 Mg/Kg in shrimps (Fig. 2a). Contrarily, water had the highest concentration (1.50 Mg/L) of Cd, compared to 0.85 Mg/Kg in sediment and 0.27 Mg/Kg in shrimps (Fig. 2b). Levels of Lead (Pb) in the study samples followed a similar trend like that of Cd. The highest concentration of Pb was obtained in the surface water samples (16.05 Mg/L) in March (Fig. 2c). This was followed by the sediment with a mean concentration of 11.2 Mg/Kg and the least mean concentration was in the shrimps (4.21 Mg/Kg). As observed in Fig. 2d, Ni concentration was elevated more in the sediment (36.63 Mg/Kg) than in the water (13.19 Mg/L) and in the shrimp (7.06 Mg/Kg), but zinc followed a contrary pattern whereby shrimps had the highest concentration of 65.35 Mg/Kg in July. The concentration of Zn in sediment was 48.70 Mg/Kg while that of water was 19.57 Mg/L in November (Fig. 2e).The mean Cu concentration was higher in sediment (37.52 Mg/Kg) in October (Fig. 2f) than in water (24.72 Mg/L) and in shrimps (13.05 Mg/Kg).

Of all the metals studied, iron (Fe) was found to be the most abundant heavy metal in Iko River Estuary. Although levels of Fe were generally high in all the samples studied Fig. 2g), concentration in sediment (113.99 Mg/Kg) far outweighed the concentrations in shrimps (227.11 Mg/Kg) and in water (184.35 Mg/L). The highest concentration of Mn (41.99 Mg/Kg) was observed in the sediment, while the values in water and shrimps were 17.82 Mg/L and 16.94 Mg/Kg respectively (Fig. 2h). Similarly, Fig. 2i showed that Vanadium (V) concentration in sediment (6.97 Mg/Kg) was higher than those of water (4.80 Mg/L) and shrimp (1.95 Mg/Kg).

The levels of heavy metals determined in the water, sediment and shrimps showed variations during the wet and dry seasons (Table 1). The Cr value was generally high in the dry season and low in the wet season in the shrimp, water and sediment, whereas Cd values were higher during the wet season than in the dry season. Mean Cd concentration during the wet season were: 0.37 Mg/L, 0.45 Mg/L and 0.18 Mg/L for water, sediment and shrimp respectively. Lead (Pb) concentration was higher in the dry season than in the wet season with highest concentration recorded in water (14.73 Mg/L) than in sediment (11.05 Mg/Kg) and shrimp (3.68 Mg/Kg). The Ni values were higher during the dry season than in the wet season with the highest value of 32.70 Mg/Kg recorded for sediment. Mean Ni dry season value for water and shrimp were 11.87 Mg/L and 5.72 Mg/Kg respectively.

For Zinc (Zn), highest value of 50.19 Mg/Kg in shrimp was recorded in the wet season. This was followed by a higher value in water (49.46 Mg/L) and sediment (38.10 Mg/Kg). Generally, Zn recorded higher values in wet than in dry season. Similarly, Copper (Cu) recorded higher wet season values than its dry season counterpart. Highest concentration of 33.01 Mg/Kg was obtained in sediment while lower concentration of 17.25 Mg/L and 11.66 Mg/Kg were recorded for water and shrimp respectively. The values of iron (Fe) recorded in the wet season were higher than values recorded in the dry season. Sediment recorded the highest Fe concentration (1005.56 Mg/Kg), followed by shrimp (211.21 Mg/Kg) and water (158.28 Mg/L). However, wet season values for manganese (Mn) were greater than the dry season ones. Mean concentrations of Mn for water, sediments and shrimps were 15.42 Mg/L, 37.37 Mg/Kg and 14.71 Mg/Kg respectively for the wet season while the dry season values were 6.90 Mg/L, 26.57 Mg/Kg and 7.17 Mg/Kg for water, sediments and shrimps respectively.

Again, sediment recorded the highest concentration of 37.37 Mg/Kg; this was followed by water (15.42 Mg/L) and shrimp (14.71 Mg/Kg). Furthermore, vanadium (V) concentrations were higher in dry season than in the wet season. Levels of vanadium in sediments were higher (5.14 Mg/L) than values in water (3.57 Mg/L) and in shrimp (1.56 Mg/Kg).

4. DISCUSSION

Heavy metals have been used as indices of pollution as water bodies have been subjected to contaminating materials which is capable of causing impairment of the quality of an aquatic ecosystem. The study found that the mean concentration of Chromium (Cr) in surface water exceeded the USEPA [17] recommendation of (0.1 mg/l^{-1}) and WHO [18] acceptable limits of (0.5 Mg/L). The results in this study is similar to the report of Umoren et al. (2012) (0.009 - 0.345 Mg/L) on Qua Iboe River, but is at variance with the findings of Essien et al. [14] (0.02 Mg/L) for asphyxiated mangrove ecosystem of Qua Iboe River Estuary and that of Ndimele and Kumolu-Johnson (2012) (0.01 Mg/L) for Badagry Creek. The low levels of Cr during the wet season could be as a result of dilution due to the influence of water waves in the estuary. Chromium, though an essential micronutrient for animals and plants, can be toxic in excess amount especially in the hexavalent form. Long-term exposure can cause kidney, liver, circulatory and nerve tissue damages. Chromium often accumulates in aquatic life, adding to the danger of eating fish that have been exposed to high level of Chromium [19,20]. Nevertheless, in this present study, the concentration of chromium (Cr) in the shrimps fluctuated widely in all the stations with mean value of 0.20 Mg/Kg beingbelow the FAO/WHO [21] accepted levels. Sources of Chromium permeating the environment are air, water erosion of rocks, power plants on liquid fuels, brown and hard coal, industrial and municipal waste [22]. Chromium is currently banned in sea food in the developed countries. The carcinogenicity of hexavalent Cr to man and other mammals and the prevalent use of this metal in the leather and textile industries provide sufficient motivation for the continued monitoring of shell fish for this metal [23].

The mean concentration of Cadmium (Cd) (0.27 mg/l^{-1}) recorded in this study was above the maximum allowable level of 0.005 Mg/L by USEPA [17] and 0.003 Mg/L. Cadmium is known for showing very high toxicity to both aquatic and terrestrial organisms even at low concentrations [24] The range of Cd (0.19 - 0.38 Mg/L) observed in this study disagrees with the range (0.028 - 0.063 Mg/L) obtained by Aghoghovwia et al. [25] in Warri River, Niger Delta. Seasonally, higher wet season values (0.3 7± 0.22 Mg/L) than dry season (0.12 ± 0.11 Mg/L) could be adduced to run off from industrial effluents within the river catchment. This finding corroborates the report of Mondol et al. [26]. Cadmium is toxic even at low concentration; and chronic exposure to high levels of Cadmium in food has caused bone disorders, including Osteoporosis and Osteomalacia. Cadmium is known to cause itai-itai; this disease causes pains in the back and joints, bone fractures and occasional renal failure, and most often affects women with multiple risk factors such as multiparity and poor nutrition. Other consequences of cadmium exposure are: aneamia, yellow discoloration of the teeth, damage to the olfactory nerve and anosmia [27,28]. In this present study, mean concentration of 0.12 Mg/Kg recorded in the shrimps was above the FAO/WHO [21] permissible limits of 0.5 Mg/Kg in fish and fishery products.The range of cadmium (0.10-0.15 Mg/Kg) recorded was consistent with the range (0.003-0.18 Mg/Kg) reported by Vincent-Akpu and Babatunde [29] for Elechi-creek, but was at variance with the range (0.90-1.18 Mg/Kg) reported by Nwabueze [30] for creeks in Burutu in Delta State. Human are exposed to cadmium through food intake and the average daily intake for adults was put at approximately 50 mg [31].

Lead (Pb) is highly toxic, very common and is harmful even in negligible quantity [32]. The mean concentrations of Pb (14.73 Mg/L) in water were high and this could be due to the cumulative effect of exhaust emissions from automobiles which finds its way by surface runoff into the estuary. The results obtained showed higher values when compared with values reported by Emoyan et al. [33] (0.025 - 0.058 Mg/L) for River Ijana Ekpan, Wegwu and Akininwor [34] (0.85 Mg/L) for New Calabar River, Port Harcourt and Akporido [35] (0.039 Mg/L) for Esi river. Mean Pb values in this estuary far exceeded the WHO tolerance level of 0.01 Mg/L for portable water. Seasonality regime revealed higher dry season value (14.73 ± 3.61 Mg/L) than its wet season counterpart (11.42 ± 2.17 Mg/L). The level of Pb (2.62 Mg/Kg) in the shrimp samples were above the recommended 1.5 Mg/Kg stipulated by FAO/WHO [21]. Higher Pb levels above standard safe limits had been reported by Mitra et al. [36] for River Ganga, India. Higher dry season value than wet season corroborates with the report of Jimoh et al. [37]. Emissions from burning of fossils fuels, dust from lead paints and waste gases from leaded gasoline could be implicated in the high load of lead in the dry season.

Lead (Pb) is considered the number one health threat to children, and the effects of lead poisoning can last a lifetime. Children can be seriously lead poisoned during renovations, modeling and construction activities in the house or class that contains lead paints. Not only does lead poisoning stunt a child's growth damage the nervous system, and cause learning disabilities, but also it is now linked to crime and anti-social behavior in children [38]. Furthermore, high concentration of lead in the body can cause death or permanent damage to the Central Nervous System, the brain and kidneys (Hanaa et al., 2000). Zamfara lead poisoning is the worst and most recent heavy metals incidence in Nigerian records that claimed over 500 children within seven months in 2010 [39].

Nickel is regarded as an essential heavy metal but toxic in large amount to human health. Nickel is used as alloys product, nickel-plating for anticorrosion and in the manufacture of batteries. The mean concentration of Nickel (Ni) ranged from 6.38 - 11.86 Mg/L. Values obtained surpassed the tolerance limit (0.02 Mg/L) set by WHO [18]. Source of elevated Nickel load could be traced to cumulative effect of petroleum substances (petrol, diesel and engine oil) from motorized boats used for commercial activities in Iko River Estuary. Mean result obtained exceeded the range (0.030 - 0.080 Mg/L) reported by Emoyan et al. [33] for River Ijana, Ekpan and 0.22 - 0.45Mg/L [40] for River Owan, Edo State. Nickel concentration during the dry season (11.87 ± 3.22 Mg/L) was higher than that of the wet season (7.23 ± 2.74 Mg/L) and this result was similar to values 5.17 ± 1.73 Mg/L and 7.41 ± 1.31 Mg/L for dry and wet season respectively as reported by Dan et al. [41] for Qua Iboe River Estuary. The mean value of Nickel (3.94 Mg/Kg) was far below the FAO/WHO [21] threshold value of 80 Mg/Kg. Nickel is a hazardous metal notified by the USFDA [42]. However Nickel related health effects have been reported to include worsening of eczema (Kaaber et al., 1979), hair loss (Hanaa et al., 2000) as well as renal, cardiovascular, reproductive and immunological effects [43].

Accordingto the WHO [18], the maximum allowable level for Zinc is 3.0 Mg/L but the mean concentration of Zinc (44.02 Mg/L) obtained in this study was above the maximum allowable limit. This high level of Zinc may not be unconnected with Zinc particles from suspended domestic wastes including sewage and roofs of houses within this vicinity. However mean concentration of Zinc obtained in this study was contrary to the report by Ideriah et al. [44] (0.2098-0.1208 Mg/L) along Abonnema Shoreline, Nigeria; (0.002-0.050 Mg/L) reported by Aghoghovwia et al. [24] on Warri River, Niger Delta and (0.09-0.12 Mg/L) by Enuneku et al. (2013) on River Owan, Edo State. The high Zinc concentration in wet season (49.46 Mg/L) than dry season (36.41 Mg/L) could be linked to increased precipitation in the wet months resulting in an overflow of local sewage pipes and increased input. This supports the assertion by Muniz et al. (2004) that Zn is frequently associated with sewage. Earlier report by Emoyan et al. [33] on River Ijana in Ekpan-Warri, attributed their high Zinc level to the high concentrations of cadmium and Iron in that zinc occurs in nature with other metals of which iron and cadmium are the most common. In shrimp, Zinc concentration varied between 11.02 - 54.60 Mg/Kg and was above the maximum allowable limit of 30 Mg/Kg according to FAO/WHO, [21]. This range was not in agreement with the report of Oguzie and Achegbulu (2010) (0.196 - 0.452 Mg/Kg) for Ovia River but compares favourably with the report of Mitra et al., [36] (31.23 - 98.10 ppm). Zinc is one of the important trace elements that play a vital role in the physiological and metabolic processes of many organisms. Nevertheless, higher concentration of Zn can be toxic to the organism [45].

The proportion of copper decreased during the dry season (8.68 Mg/L) but increased during the wet season (17.25 Mg/L); and this may be due to mineral weathering and runoff from industrial, agricultural and residential land uses. Higher concentrations of toxic heavy metals in riverine sediments may pose ecological risks to benthos [46]. This corroborated with the report of Ewa et al. [47]. Mean copper level (13.68 Mg/L) was quite high compared with values (0.07 Mg/L) reported by Ideriah et al. [44] and 0.020 Mg/L recorded by Emoyan [33], also Cu levels exceeded the WHO Guidelines value (2.0 Mg/L) as well as USEPA (2012) value of (1.3 Mg/L).This study found that copper levels in shrimps varied between 6.74-11.72 Mg/Kg. However, these values though high, did not exceed the limit of safety (20 Mg/Kg) for human consumption [21]. Contamination of drinking water with high level of copper may lead to chronic anemia (Archarya et al., 2008). Copper is one of the most toxic metals to aquatic organisms and ecosystem and it is moderately soluble in water and binds easily to sediment and organic matter. In his study on the impacts of copper on aquatic ecosystems and human health, Solomon [48] averred that fish and crustaceans are 10 to 100 times more sensitive to the toxic effects of copper than are mammals, and that algae especially blue-green algae species are 1,000 times more sensitive to the toxic effects of copper than mammals.

The Fe content across the course of the Iko River Estuary was generally high and far exceeded the USEPA recommended bench-maker (0.3 Mg/L). High concentration of Fe above the USEPA recommended threshold value have been reported in Nigeria Territorial waters by Nubi et al. [49], Chellawa Gorge dam, Kano by Malami et al. [50], and Dan et al. [41] for Qua Iboe River Estuary adjourning creeks. However, lower concentration of Fe in water than values obtained in this study has been reported by Emoyan et al. [33] (0.050 Mg/L for River Ijana in Ekpan); Ndimele and Kumolu-Johnson (2012)

(0.038 Mg/L for Badagry Creek); and Aghoghovwia et al. [25] (0.3-0.7 Mg/L for Warri river, Niger Delta).Seasonality profile revealed higher wet season concentration (158.28±36.50 Mg/L) which could be attributed to surface run-off and anthropogenic inputs. Noteworthy in shrimps is the consistent higher concentration of iron than other metals in this study. High concentrations of iron (Fe) in shrimps demonstrate an evidence of bioconcentrationof Fe by the shrimps. However, excess waterborne iron may be toxic to fish, due to the formation of iron "flocs" on the gills, resulting in gill clogging and respiratory perturbations [51]. Iron is regarded as the fourth most abundant element by mass in the earth crust [52], and is generally present in a ferric state (Fe^{3+}) in water. Prolonged consumption of drinking water with high concentration of iron may lead to liver disease known as haemosiderosis, while shortage of iron causes anaemia [53,54]. However, no guideline is set by WHO [18] for iron content in drinking water because it is not of health concern at concentrations normally observed in drinking water.

The mean value of manganese (11.84 Mg/L) in this study was found to be higher than the WHO maximum permissible level of 0.5 Mg/L. Increased wet season concentration (15.42 ± 3.93 Mg/L) than dry season (6.90 ± 2.32 Mg/L) could be traced to run-off from industrial effluent and anthropogenic inputs. High wet season manganese concentration than dry season had earlier been observed in Calabar River by Ewa et al. [47]. The range of value of manganese (Mn) (8.84 - 15.43 Mg/Kg) in shrimps for this study was above the recommended statutory limit (1.0 Mg/Kg) by FAO/WHO [21]. Higher manganese values (69.36 - 94.61 Mg/Kg) in shrimps was also reported by Adediji and Okocha, [55] from Epe Lagoon and Asejire River in South West Nigeria. Manganese is an essential element for both animals and plants. Deficiencies of Mn result in severe skeletal and reproductive abnormalities in mammals. It is widely distributed throughout the body with little variation and does not accumulate with age [56]. Additionally, manganese is essential for bone structure, in reproduction and for the normal functioning of the nervous system [57-78].

Low concentration of vanadium was observed with a mean value of 2.48 Mg/L. Higher concentration was observed during the dry season (3.57±1.0 Mg/L) than the wet season (1.70±0.79 Mg/L). Low levels of vanadium in this study indicated that this metal is only present in negligible quantity. Undetected vanadium concentration was reported by Ewa et al. [46] in their work on seasonal variations in heavy metals status in Calabar River.

5. CONCLUSION

Trace metals analyzed in water, sediment and shrimps included cadmium, chromium, lead, nickel, zinc, copper, iron, manganese and vanadium. Sediment analysis indicated elevated concentrations of these metals except Zn which was higher in shrimps than in water and sediment. High levels of heavy metals in shrimp indicated that the pollution was at hazardous levels for the health of human thus posing future dangers. The variation in levels of heavy metals in the sediment, biota and the overlying water column of the river showed the concentrations were influenced by nearness to abandoned oil facilities as well as seasonal changes. From this study, levels of heavy metals detected in pelagic column, biota and sediments seemed to have come from human-mediated sources.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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