Heavy Metals Concentration as a Determinant of Surface Water Quality; a Case Study of Asaba

Chukwu Kevin Ejike Ph.D.
Department of Geography and Meteorology, Faculty of Environmental Sciences, Enugu State University of Science and Technology (ESUT), Enugu, Enugu State, Nigeria

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*Corresponding author
Chukwu Kevin Ejike

Abstract: This work is aimed at examining the effect of heavy metal concentration on surface water quality. This study was concentrated on the lower Niger River from Illah through Asaba/Onitsha to Okpai (Lat 6° 25' to Lat 5° 40' N and longitude 6° 37' to 6° 47' E). The data collected from water and were analyzed for the heavy metals (Zn, Cu, Pb, Cd, Ni, Fe, Mn and Co) using urican 929 Atomic Absorption Spectrophotometer. The results showed that Turbidity, BOD, TSS, hydrocarbon, coliform, magnesium and iron concentrations in the sampled settlement did not meet the WHO (2010) threshold for drinking water quality. The following conclusions were reached; the Niger River water must be treated before drinking, to remove or reduce the amount of non-essential or essential heavy metal and eating of fish species that have bio-accumulated heavy metals above the WHO limits for consumption must be prohibited or discouraged. Also, further studies should be carried out to monitor the heavy metal concentration in the lower Niger River and to identify the point sources of entry; and various contributors to the contamination of the River Niger. Heavy metals have however been grouped into two categories – Essential and Non-Essential. Zinc, Iron, Manganese, Copper and Cobalt are essential and beneficial elements but become toxic when their concentrations exceed those required for normal life Lead, Arsenic, Beryllium, and Mercury are non-essential and are not required in biological systems because they are toxic. The following recommendations were made; frequent environmental monitoring (at least twice a year) must be conducted to know levels of heavy metals contamination especially of the aquatic systems; Education of the neighbouring populace on protection of the environment through various technical programmes may very useful; The Niger River water must be treated before drinking, to remove or reduce the amount of non-essential or essential heavy metal such as Cr and Fe; The eating of fish species that have bio accumulated heavy metals above the WHO limits for consumption must be prohibited or discouraged; Further studies should be carried out to monitor the heavy metal concentration in the lower Niger river and to identify the point sources of entry; but, the result of this study should form the baseline data for the assessment of the various contributors to the contamination or otherwise of the River Niger. Thus, the pollution trends in the future can easily be monitored.
Keywords: Heavy metals concentration, Determinant, Surface water quality, Asaba

INTRODUCTION

Man, the social animal, is always at logger heads with nature in favour of economic and technological advancement and rivers and fish are not spared in the process [1]. Human destructive influence on the aquatic environment due to discharge of pollutants, results in chronic stress conditions with the attendant negative effect on aquatic life. While the demand for fish protein is increasing astronomically with growing population, the rivers are being reduced to sewage dumps with pollutants killing fish and other aquatic organisms. Increase in industrialization, growing human population, oil exploration and exploitation has been implicated for increase of Man-made pollutants in the aquatic environment and has subjected it to enormous ecological degradation.

One key adverse environmental impact of heavy metal contamination of the sediment and water column in lagoon, riverine and marine settings is the

potential for the transfer of toxic metals into the food chain. Indeed many scientists should be familiar with the minamata bay disaster in Japan where Mercury contamination and subsequent assimilation of Mercury by aquatic organisms resulted in Mercury poisoning including the death of many local people, mainly fisher folk. This example is an extreme case of assimilation of toxic trace metals but other very serious incidents of Mercury assimilation have been reported in the Gulf of St Lawrence, Canada [2] and Chromium and Cadmium poisoning have been documented in Japan. In contrast to the relatively recent recognition of the consequences of Hg and Cd assimilation, health disorders in humans including brain damage and mental deficiency, promoted by the direct bioaccumulation of Pb have been recognized for millennia [3].

Heavy metals are generally and naturally found at very low concentrations normally at the nanogram or microgram per liter but in recent times, the occurrence of heavy metals in excess of natural loads has become a problem of increasing concern [4] while elevated concentrations are commonly associated with pollution from human activities [5].

Heavy metals have been defined as metals having density more than $5g/cm^3$ and with atomic weight of 40g and above [6, 7] or a metal with atomic mass greater than that of Calcium [8]. Heavy Metals cannot be degraded biologically and are easily assimilated and bio accumulated into the protoplasm [9]. They are inorganic elements essential for plant growth in trace quantities but become toxic in relatively higher concentrations. The heavy metals are known to occur naturally in ores, usually as a combination of several metals in organic or inorganic forms and their release to the environment is almost entirely from the ores such as Sphalaerite or Galene (a combination of Zn and Cd) and (a combination of Iron and Chromium) respectively.

Heavy metals are found in natural waters as particulates or soluble inorganic or organics. The soluble forms occur as free aquatic ions, complexed ionic entities, inorganic ion pairs or complexes, organic complexes, chelates compounds, molecules or as metals bound to high molecular weight organic materials. On the other hands, particulate metals could be colloidal, sorbed or suspended. Metals appearing in different chemical forms have different characteristics and different affinities to various carrier particles existing in natural water system [10]. Carrier particles may camouflage toxic properties and govern the spread of metal species in nature and these include mineral detritus, clay minerals, humic substances, bitumen, lipids, residual organics, hydrous iron and manganese, oxides and carbonates [11]. There are generally five sources of heavy metals in surface waters and these are from geographical weathering, animal/human excretion,

garbage/solid waste, processing of ores and metals as well as from the use of metals and metal bearing compounds. Geographical weathering is the source of background levels and areas characterized by metal bearing formations have these metals occurring in high level in the waters. Fufeyin [11] explained that heavy metals are present in human and animal food in relatively high concentrations and such heavy metals find their way into the aquatic environment through direct or indirect dumping. Heavy metals are leached from Garbage and solid waste dumps and these can be a very serious source of pollution in the aquatic environment. Metal- bearing dust particles are found during the processing of ores and appreciable quantities of metals end up as waste in the process of galvanizing or other chemical metal refinement methods. Various industries use metals and metal compounds widely;. For example Chromium Salts are used in the tanning industry while Copper compounds are used as plant protection agents and tetramethyl lead as anti – knock agent. Also many heavy metals are used in metallurgy, electrical contact batteries, and nuclear reactor control rods and in pigment compounds to give brilliant yellow and orange colours to paints, ceramics and glass. Van de Broek [12] and Barcellos *et al*., [13] explained that effluents from the aforementioned industrial processes as well as atmospheric emissions, river transport and discharge of sewage and dredged spoils end directly through smaller streams into bigger Rivers.

Ntekim *et al*.,[14] in their investigation of the Calabar River reported that the concentration of Pb, Zn. and Cu indicated relative moderate pollution while concentrations of Ni, Cr, Co, Cd and Fe were below values of adverse effects on the lives of the biota. This study also observed that the enhanced heavy metal concentrations were related to industrial sewage, metal leaching from garbage and solid waste dumps all of the studies so far in Nigeria have not taken into consideration the partitioning of anthropogenic heavy metals to the water, Bottom sediments and fish of the river reported.

AIMS AND OBJECTIVES
The main purposes of this research are:
- To determine the surface water quality Vis a Vis the heavy metals concentration of the rivers in Asaba and its environs. (Surface water and bottom sediments).
- To examine the influence of long term domestic waste and industrial effluent discharges ,agricultural run-off and other anthropogenic inputs on the pollution of surface water in Asaba and its environs in lower Niger River.
- Also, to establish the baseline for the heavy metals deposited in the water, bottom sediments in order to monitor heavy metal pollution trends in the future.

LITERATURE REVIEW

Heavy metals enrichment in aquatic systems have been frequently attributed to industrialization, urbanization and high human population density due to the discharge of effluents, wastes and domestic sewage to the aquatic bodies directly and through rainwater run-off [15-23, 11, 24, 25].

Effects of Heavy Metals in the Rivers and How Its Effect Man

The Niger River serves as a source of drinking water and protein to the inhabitants along the banks and environment. Although some of the metals are still below the WHO recommended levels, continuous introduction of these heavy metals through anthropogenic sources will lead to serious pollution of the river. It is known that many heavy metals are toxic to aquatic organisms but the exact modes of actions are unknown and the levels at which they become harmful are still under investigation. Oronsaye [26] observed that metals are easily chelated by organic molecules and may become combined with the cell membrane to effect permeability. Fufeyin [11] explained that early investigators of pollutant effects on fish attributed their death when exposed to lethal heavy metal concentrations to coagulation and precipitation of mucous on the gills resulting in death by suffocation. Later, cytological damage rather than mucous accumulation was cited for the increased diffusion distance between water and blood. Mallat [27], Evans [28], Spicer and Weber [29] reported that acute exposure to heavy metal results in profound changes in ultra-structure of the crustacean gill and possibly in the production of mucous on the surface water bodies.

The uptake of heavy metals has severe adverse effects on growth and development as well as the quality of fish from the river. The continuous use of fish as a source of protein could lead to the accumulation of these heavy metals in man. Man has been reported to have the ability to reject some of the injected metals but small quantities are retained and accumulate over the years until threshold levels are attained. The health effects of these lethal levels of heavy metals cannot be over-emphasized. However, they could be better appreciated of treated on individual heavy metal basis thus;

Zinc (Zn)

High Zn concentration increases coughing frequency as well as ventilating aberration causing reduction in amount of O_2 available to the tissues-hypoxia [30].
As for man, taking more than 100mg of Zn depress the immune systems; and, accelerates the growth of prostate and colon cancer. Excessive intake of Zn by man result in vomiting, nausea, diarrhea, stomach ache, poor muscle coordination, fatigue and possible kidney failure.

Cadmium (Cd)

Cd has serious health effects on man when he is exposed to it. It accumulates in organs like liver, kidney and pancreas. Acute high exposure causes severe respiratory irritation, lung disease (through air borne exposure), and testicular degeneration [31]. Cd destroys a specific structure of the functional unit of the kidney (proximal tubules of each nephron) in a way that is first manifested by leakage of low molecular weight proteins and essential ions such as Ca into urine leading to kidney failure over a time [32]. Loss of Ca leads to weakening of bones.

High blood pressure, liver damage, destruction of red blood cells, bronchitis, cancer, epithelium necrosis (death of tissue lining the lungs) inactivated enzymes; abdominal swelling of lungs (emphysema) abdominal pains, nausea, vomiting, dizziness, and diarrhea are some of the common diseases caused by Cadmium (Cd) [33, 7, 25].

The toxic effects and bio pathology of Cd in animals and humans have reviewed by Flick *et al.,* [34]. According to them, in sufficient concentrations, Cd may exert its toxic effects on fish by coagulating external gill mucus, causing anoxia, altered salt balance and secretion of waste products. It also effectively poisons various fish liver enzymes and depletion of liver muscle glycogen and haemoglobin.

Hiltibran [35] reported that at relatively low levels, Cd disrupts energy production by severely limiting oxygen uptake by excessive mucus secretions and fusing of gill lamellae. Oronsaye [26] also reported a general depression of feeding and growth rates of fish. The human body was reported to be unable to eliminate absorbed Cd and hence all efforts should be made to reduce Cd contamination to the barest minimum. Copper (Cu) Cu is essential to the body of man and the adult daily requirement is about 2.0mg. Large oral doses produce emesis and results in liver damages. It gives bitter taste to water at a concentration greater than 1.0mg/l and tends to absorb on surfaces of containers. In general, excessive intake results to stomach and intestinal distress leading to vomiting, diarrhoea, stomach cramps and liver disorders.

Fresh water fish are rapidly killed by less than 1ppm as fish absorb Cu through gills [36]. Iron (Fe) Fe has not been found to be acutely toxic but it imparts brown colour to fixtures and laundry and gives unpleasant taste to drinking water at levels above 1 or 2mg/l. It also reacts with sulphides lead-ins to the formation of sulphuric acid in water. The presence of the acid in water leads to oxygen deficiency and this has been identified as one of the main causes of fish kills in the United States of America [37]. Massive fish kills can also occur when Fe and Al are mobilized with

drainage from acid sulphate soils [38]. Excessive accumulation of Fe promotes bacterial growth as Fe is needed for their growth. It also causes cancer and more than 0.1mg/l precipitates after exposure to air causing turbidity, stains to cooking utensils and laundries [39].

Manganese (Mn)

Mn is not toxic to human in low concentrations but could impart objectionable stains to laundry and plumbing fixtures. High level of Mn intake may be mutagenic and Parkinson disease has been associated. Excess Mn causes decrease in white and red blood cells, haemoglobin, and plasma sodium and protein concentrations [40]. It was reported by Bond *et al.*, [39] that more than 0.2mg/l of Mn precipitate upon oxidation causing undesirable tastes and deposits on food during cooking.

Nickel (Ni)

Ni may not be acutely toxic to humans but chronic accumulation in man results in paralysis, cancer and death in severe cases. In fish, it was reported by Sreedevi *et al.*,[41] to bind to affinity sites of DNA molecules to produce some conformational changes. In excess, it interferes with the detoxification activities of the liver. Ni may be harmful in survival and productivity of freshwater fauna especially fish and shellfishes thereby disturbing the natural ecosystems and food chains. Ni causes allergic reaction leading to asthma. It can cause bronchitis, kidney and liver cancer. It can also cause headache, dizziness, nausea, vomiting, chest-pain, tightness of the chest, dry cough, with shortness of breath – rapid respiration, cyanosis and extreme weakness. It also causes lesions mainly in lungs and brain [42].

Chromium (Cr)

Anaemic conditions occur in fish resulting in decreased oxygen utilization and hypoxia (reduction of oxygen going to the tissues). The presence of Cr leads to decreased metabolism and decrease in blood pH [40]. Hexavalent chromium compounds are irritating and corrosive when absorbed through the digestive track, skin or lungs of man. Inhalation of dust or mists irritates the upper respiratory passage of man leading to sneezing, nasal discharge and congestion.

RESEARCH METHODOLOGY
RESEARCH DESIGN

Survey research design was adopted in the study. The present research was a survey because the subjects were investigated in their natural settings.

Area Study

The Niger River is the principle river of West Africa, extending over 2500 miles (about 4180kms). It runs in a crescent through Guinea, Mali, Niger, on the border with Benin and then southwards through Nigeria. Rising in Guinea (just 150 miles (240kms)

inland from the Atlantic Ocean), the river flows northeast into Mali, running away from the sea into the Sahara desert. East of Timbuktu, it bends to southeast, flowing across western Niger and forming part of the international boundary between Niger and Benin. The Niger River is therefore said to have one of the most unusual routes of any major river, a boomerang shape. The most important tributary of the Niger River is the Benue River which merges with it at Lokoja in Nigeria. The Niger River then flows predominantly southwards from the confluence with the Benue and finally discharges into the Gulf of Guinea through a network of outlets that constitute an extensive Delta known as the oil rivers. This study is concentrated on the lower Niger River from Illah through Asaba/Onitsha to Okpai (Lat 6° 25' to Lat 5° 40' northings and longitude 6° 37' t0 6° 47' easting's). The secondary rainforests along the catchment areas have been subjected to extensive land clearing and farming activities, and as a result the river receives a lot of agricultural waste, through runoff from bordering agricultural lands. A lot of wastes from industrial and domestic activities in and around the fast growing town of Asaba and highly urbanized town of Onitsha as well as surrounding villages of Okoh, Anwai and Ugbolu are all emptied into the river. The Grand hotel, the Ogbonogo market, the Federal Medical Centre, Mami market, Cable market and Delta textile mills Asaba are some of the known contributors to the pollution of the river. Metal fabricators along the catchment areas are involved in the production of car rims, iron beds, cutlasses, pots, underground and surface tanks etc, in and around Asaba/Onitsha axis of the river catchments and are some of the major contributors to the Heavy Metal pollution of the river. During the rains, some of the waters enter the river through runoff and sewage, while others are dumped directly. The study area is underlain by three subsurface depositional structures, namely the Benin, Ogwashi-Asaba and Ameki formations. The Benin formation immediately underlies the Asaba terrain and extends from surface to about 59m. It is composed of pinkish to whitish, medium to coarse grained sands and lenticular clay [43]. Below the Benin formation lies the Ogwashi-Asaba formation which extends from 59m to 180m.it also extends laterally to neighboring towns of Ibusa, Okpanam and Azagba Ogwashi -Uku where it is thickest. Strategically the formation is characterized by alternation of sand, lenticular sandstones, clay, shales with subordinate sandstones and lignite. In some places such as at Ibusa and Azagba-Ogwashi-uku the lignites even grade into coal. The third formation that underlies the Asaba terrain in a descending order of depositional episode is the Ameki formation. This is the most important aquiferous formation and also extends across Onitsha and beyond. It is generally very permeable with the coarse grained sands being recharged by the river Niger. The above geologic features also cover the Illah environment of the lower Niger River and fall within the Onitsha sombreiro. Okpai area is however part of

the sombreiro of Warri Deltaic plain and represents the remnants of a Delta which was formed in late Pleistocene to early Holocene times and later was largely eroded away [44]. This area is overlayed by the sandy Benin formation up to 200m in thickness and is influenced by a continuous interplay between subsidence and deposition. Sand, silt, clay and organic rich sediments are complexly interbedded to form lithofacies. The climate can be said to be stable but not uniform. It has two distinct seasons, the rainy season and the dry season. The timing however varies from year to year. The rainy season during the period of study lasted from April to October and an august break in August / September. The dry season extended from November to March but was interrupted from December to January by the dry dusty harmattan season. The harmattan season in Asaba station however extended to early February. The mean annual rainfall in Asaba sombreiro was 155.3 inches and at the Warri sombreiro which covers the Okpai station, the mean annual rainfall was 255.7 inches.

Sample Stretch

This research was limited to the lower Niger river and three sampling stations were chosen. these stretch from Illah through Asaba/ Onitsha axis down to okpai (the gas gathering project site. the sampling stretch rests within latitude 6° 25' and 5° 40' northings and longitude 6^0 37 to 6^0 47 easting. these sampling stretches were characterized by flowing water and were much affected by surface run off during the raining season from the catchment areas of the river especially in the Asaba/Onitsha station where various developmental projects were on the rise. aside this, much of the shore areas of the sampling stretch were flooded in the raining season.

Water Studies, Collection and Pre-treatment

On each sampling day, surface water samples were collected in pre-treated polypropylene sample bottles at an approximate depth of 30cm below the water surface using a hydro bios water sampler. Water samples were immediately preserved by acidifying with concentrated nitric acid (HNO3 analytical grade) to $P^H<$ 2 [45]. After acidification of the samples, they were stored in an iced cooler in the field and later transferred to a refrigerator at approximately 4^oC to prevent change in volume due to evaporation. Water samples for chemical analysis were also collected in sample bottles without fixing with acid and treated like other samples in a refrigerator.

Pre-treatment and Digestion of Water Samples

The water samples that had already been fixed in Nitric Acid were filtered through what man filter paper No. 1 and aspirated directly into the AAS for heavy metals such as Cd, Cu, Pb, Mn, Ni Cr, Co and Zn.

Determination of Iron by the Phenanthroline Method

The concentrations of iron in all samples of water, bottom sediments and fish were determined by the 1 -10 Phenanthroline method of APHA [45] 2mls of the digestate was put in a flask. 2mls of 1 -10 Phenanthroline, 20mls of sodium citrate and 2mls of hydroxylamine hydrochloride was added. This was mixed thoroughly and left to stand for two hours. The percentage absorbance was read off from a spectrophotometer at 465nm wavelength. Iron concentrations were determined from the standard curve.

Preparation of Standard Curve

The standard stock solutions were prepared by dissolving various amounts of 1ppm, 5ppm, 10ppm and 20ppm, 40ppm of dried annular grade Iron nitrate in distilled water. The percentage absorbance of each standard solution was measured and the calibration curve drawn for the different concentrations. A blank sample was prepared using distilled water.

Bottom Sediment Studies

Samples of the bottom sediment were obtained from each station for the period with the aid of bottom sediment 'Eckman Grab' attached to a polypropylene rope. The samples were immediately placed into plastic bags and cooled in an iced cooler in the field and later transferred to the refrigerator in the laboratory prior to analysis. The samples were pre – treated of debris and dried at 105^oc in a moisture extraction oven. The dried samples were then passed through 100mm mesh sieve and stored in plastic bags [20]all containers used were soaked in 30% Nitric Acid for 84 hours and then rised with deionized water. When not in use, the glassware's were stored in deionized water acidified with Nitric Acid to a P^H of 3. All reagents used for analysis were of the analytical grade and fresh supply free from trace metal contamination.

Percentage Organic Matter Content

The total organic matter contents of the sediments were estimated from the percentage loss on Ignition as described by Allen [46]. 1g of Oven dried soil was put into a pre – weighed crucible. The crucible with its contents were placed to rise slowly to 55^oC and left for 2 hours. The crucible with its contents was transferred todesiccators, cooled to room temperature and reweighed. The % loss on Ignition was calculated from the weight loss during combustion using the formula.

% loss on ignition = <u>wt. loss (g) x 100</u>
Oven dry wt (g)

Digestion of Bottom Sediment Samples

Bottom sediment samples were digested using the Nitric Acid – perchloric acid method as described

by Adams *et al*., [47]. 25g of bottom sediment sample was oven dried at 105°C to constant weight. 0.5g of the dried sample was acidified with HNO_3. 20mls $HCLO_4$ was added to the filtrate and evaporated until white fumes of $HCLO_4$ appeared. When the solution became clear, the digest was filtered with a No 40 what man filter paper and diluted to 25ml mark for analysis.

Water Analysis
Temperature
Water temperatures of the Niger River were recorded using mercury in glass centigrade thermometer. The thermometer was held in the water for 3-5 minutes and the readings (for water temperatures) were taken while the thermometer was still inside water. Air temperature readings were taken from the same spot the water temperature readings were taken but in this case outside the water of the Niger River

Conductivity
The conductivity of the water samples was determined using the Hach Model 44600 conductivity / Total dissolved solid meter (T.D.S. Meter 4076 Jenway). The conductivity was measured in μdcm.

Hydrogen-Ion concentration(P^h)
The hydrogen ion concentration (P^H) of the water samples were estimated with the aid of Hach Model (P^H) meter (or P^H meter Model 3305 Jenway)

Total solids
An evaporating dish was properly washed and rinsed with distilled, oven dried, put indesiccators to cool and then weighed (W1). 100ml of unfiltered water sample was put in the evaporating dish and evaporated to complete dryness at 150 -180° C. The dish was transferred to the desiccators to cool and then reweighed, until a constant weight was obtained (W2).

Weight of the dried sample = (W1-W2)g. The total solid in 1L of water was extrapolated using the formula (W1-W2)* 1000*10 mg/L.

Total dissolved solids
This was done like total solids except that water used were filtered through Whatman filter paper No 41.

Total suspended solids
The total suspended solid was got by subtracting the total dissolved solid from the total solids i.e.
Total suspended solids = Total solids (mg/l) – Total dissolved solids (mg/L).

Dissolved oxygen
Winkler's method as described by Mackereth [48] was used to determine Dissolved Oxygen. In the field, narrow mouthed glass-stopper 250ml bottles were used to collect water and were immediately stoppered eliminating air bubbles. 2ml each of Winkler's solution A (Manganous sulphate) and solution B (Potassium hydroxide in Potassium iodide) were added well below the neck of the bottle. With the stopper firmly replaced, the contents were thoroughly mixed.

In the laboratory, the precipitate formed was dissolved by adding 2ml of concentrated sulphuric acid, to form a golden brown solution. 100ml of this solution with 2 drops of starch indicator was titrated against 0.8N sodium thiosulphate solution. The disappearance of the initial blue-black colouration indicated the end point

The dissolved oxygen (D.O) was estimated in mg/L using equation:
D. O = Vol. of titrant *N of thiosulphate*1000 / Vol. of sample used

Alkalinity
Alkalinity was determined by titration using the method of Golterman *et al*., [49]. Phenolphthalein alkanity (P.A.) was first determined by titrating 100mls of each sample against 0.02N sulphuric acid with two drops of phenolphthalein indicator in all samples, Phenolphthalein alkalinity (P.A) was zero (i.e. samples remained colourless). Two (2) drops of methyl orange indicator was added to the colourless solution and was titrated against the acid until the appearance of a faint pink colouration.

The total alkalinity was calculated from the equation:
T.A (meq/L) = Vol. of titrant*n of acid*1000/Vol of sample used
A correction factor of 0.02 meq/L was subtracted from the value obtained as suggested by Sutcliffe *et al.,*[50] and converted to mg/L with a multiplication factor of 50

Total hardness
- The total hardness was measured using a portable field kit of total hardness (Aquamerch 8039) Gesumtharte instrument. The method is a complexometric titration with titriplex III against mixed indicator.
- The measuring cylinder was washed with the water sample and filled to the 5ml mark. with 3 drops of the indicator solution was added and the mixture swirled. The colour changed to red in the presence of hardness formers.
- The titrating pipette was used to drop the regent solution slowly to the prepared water sample. The appearance of a greenish colour indicated the end point

Rainfall
The rainfall data for Asaba and Illah sampling stations were collected from the Asaba

meteorological station during the sampling period while that of Okpai station were collected from the Warri meteorological station G.R.A Warri during the period.

Of 1 -10 Phenanthroline, 20mls of sodium citrate and 2mls of hydroxylamine hydrochloride was added. This was mixed thoroughly and left to stand for two hours. The percentage absorbance was read off from a spectrophotometer at 465nm wavelength. Iron concentrations were determined from the standard curve.

Digestions and Analysis

The method used was the mixed acid procedure described by Allen [46] and modified by Sveedevi [41].The dried fish samples were ground to a fine powder in a porcelain mortar. 1g of each sample was used for digestion using perchloric – nitric – sulphuric acid method in the ratio of 1:5:1 [41]. Digestion was completed by the appearance of dense white fumes and colourless solution. The solution was filtered through what man filter paper No. 42 into 50mls volumetric flask and made up to mark with deionized water. The solution was then analyzed for the heavy metals (Zn, Cu, Pb, Cd, Ni, Fe, Mn and Co) using urican 929 Atomic Absorption Spectrophotometer.

ANALYSIS AND RESULTS
Heavy metal concentration in the bottom sediment and water (chemical Properties) at three locations (Asaba, Illah and Okpai) of Lower River Niger

Result of analysis between bottom sediments and water samples revealed that there were significant differences ($p<0.05$) between bottom sediments and water for some chemical properties of heavy metals at three locations of lower River Niger (Table-1). The highest mean values for Cr, Mn, Fe, Ni, Cu, Zn, Pb, and Cd were recorded for bottom sediment while the lowest for mean values were obtained in the water sample (Table-2). A number of scientists have been involved in investigations on the distributions and biological uptake of heavy metals in the aquatic environments. Grahn and Hakanson [10] in their studies observed more heavy metals in river bottom sediment than at water surface. Some of the properties studies were as follows:

Table-1: Effect of two treatments (Bottom sediment and water) on the concentration of Elements River

Treatment	Concentration of elements			
	CR	Mn	Fe	Co
Bottom sediment	0.34	5.59	35.27	0.06
Water	0.01	0.24	0.98	0.38
L.S.D (0.05)	0.09	1.39	11.33	0.6

Table-2: Effect of two treatments (Bottom sediment and water) on the concentration of Elements River

Treatment	Concentration of elements			
	Cu	Zn	Pb	Cd
Bottom	6.37	4.84	0.07	0.008
Water	0.39	0.28	0.01	0.001
L.S.D (0.05)	4.63	1.27	0.028	0.006

Source: Field work 2011

Findings
It was discovered that;

Turbidity, BOD, TSS, hydrocarbon, coliform, magnesium and iron concentrations in the sampled settlement did not meet the WHO [51] threshold for drinking water quality.

CONCLUSION

This study revealed that the Niger River water must be treated before drinking, to remove or reduce the amount of non-essential or essential heavy metal and eating of fish species that have bio-accumulated heavy metals above the WHO limits for consumption must be prohibited or discouraged. Also, further studies should be carried out to monitor the heavy metal concentration in the lower Niger River and to identify the point sources of entry; and various contributors to the contamination of the River Niger. Heavy metals have however been grouped into two categories – Essential and Non-Essential. Zinc, Iron, Manganese, Copper and Cobalt are essential and beneficial elements but become toxic when their concentrations exceed those required for normal life Lead, Arsenic, Beryllium, and Mercury are non-essential and are not required in biological systems because they are toxic.

RECOMMENDATIONS
- Frequent environmental monitoring (at least twice a year) must be conducted to know levels of heavy metals contamination especially of the aquatic systems.
- Education of the neighbouring populace on protection of the environment through various technical programmes may very useful.
- The Niger River water must be treated before drinking, to remove or reduce the amount of non-essential or essential heavy metal such as Cr and Fe.
- The eating of fish species that have bio accumulated heavy metals above the WHO limits for consumption must be prohibited or discouraged.
- Further studies should be carried out to monitor the heavy metal concentration in the lower Niger river and to identify the point sources of entry; but, the result of this study should form the baseline data for the

assessment of the various contributors to the contamination or otherwise of the River Niger. Thus, the pollution trends in the future can easily be monitored.

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