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Levels of heavy metal concentration in water, sediment and fish in Ikpoba River, Benin City, Edo State Nigeria

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Abstract
Ikpoba River is the ultimate recipient for municipal waste and industrial effluent in Benin City, samples of water, sediment and fish were collected at five different locations in the river for some selected heavy metal analysis in order to determine the extent of pollution. Samples were collected in June, July and August 2013. The heavy metals were determined with atomic absorption spectrophotometry (AAS). In water the heavy metal concentration were found to be in the order, Pb>Cu>Zn>Cd the mean concentration of heavy metal in the water ranged from 0.024±0.004 to 0.064±0.07mg/L, 0.022±0.002 to 0.042±0.002mg/L and 0.007±0.002 to 0.020±0.002mg/L, for Lead, Copper and Zinc respectively. Cadmium were below detection limit of the equipment used. In sediment the concentration of heavy metal were found to be in the following order Cu>Zn>Pb>Cd. The mean concentration of heavy metal in sediment ranged from 0.233±0.060 to 0.704±0.162µg/g, 0.207±0.016 to 0.432±0.041µg/g, 0.081±0.029µg/g to 0.252±0.027µg/g and 0.098±0.004 to 0.138±0.037µg/g, for Copper, Zinc, Lead and Cadmium respectively. The concentration of heavy metal in fish followed the order Zn>Pb>Cd>Cu, the mean concentration of heavy metal in the fish ranged from 0.387±0.014µg/g to 0.646±0.079µg/g, 0.247±0.057 to 0.394±0.074µg/g, 0.148±0.009µg/g to 0.176±0.006µg/g and 0.049±0.007 to 0.065±0.005µg/g for Zinc, Lead, Cadmium and Copper respectively. Most of the heavy metal determine were below the maximum permissible limit set by FEPA and WHO except Lead whose mean concentration was above the WHO and FEPA standard of 0.01mg/L for water and the maximum permissible limit of 0.3µg/g of FOA for fish.

Keywords: Ikpoba River, Heavy Metal, Fish and Sediment.

1. Introduction

Pollution of heavy metals in aquatic environment is a growing problem worldwide and currently it has reached an alarming rate. There are various sources of heavy metals; some originates from anthropogenic activities like draining of sewage, dumping of Hospital wastes and recreational activities. Conversely, metals also occur in small amounts naturally and may enter into aquatic system through leaching of rocks, airborne dust, forest fires and vegetation [1] As heavy metals cannot be degraded, they are continuously being deposited and incorporated in water, sediment and aquatic organisms [2] thus causing heavy metal pollution in water bodies. Increasing level of heavy metals in the environment from various anthropogenic sources has become a source of concern for environmentalists [3] As a result there is a need for increasing awareness of the emergency created by environmental pollution caused by human activities. Unlike the toxic organics compounds that in many cases can be degraded, the metals that are released into the environment tend to persist indefinitely, accumulating in living tissues through food chain [4] Many dangerous chemical elements, if released into the environment, accumulate in the soil and sediments of water bodies the lower aquatic organisms absorb and transfer them through the food chain to higher trophic levels, including fish. Under acidic conditions, the free divalent ions of many metals may be absorbed by fish gills directly from the water. Hence, concentrations of heavy metals (HM) in the organs of fish are determined primarily by the level of pollution of the water and food Under certain conditions, chemical elements accumulated in the silt and bottom sediments of water bodies can migrate back into the water, i.e. silt can become a secondary source of heavy metal pollution [5]

Worldwide, water bodies are the primary dump sites for disposal of waste, especially the effluents from industries that are close to them. These effluents from industries have a great toxic influence on the pollution of the water body, as they can alter the physical, chemical and biological nature of the receiving water body [6, 7] The initial effect of waste is to degrade the physical quality of the water. Later biological degradation becomes evident in terms of number, variety and organization of the living organisms in the water. [8] Often the water bodies readily assimilate waste materials they receive without significant deterioration of some quality criteria; the extent of this is referred to as its assimilative capacity [7, 9] Industrialization, like other human activities that impact on the environment, often results in pollution and degradation. Industries turn out wastes which are peculiar in terms of type, volume and frequency depending on the type of industry and population that uses the product. [10] Industrial waste is the most common source of water pollution in the present day [11] and it increases yearly due to the fact that industries are increasing because most countries are getting industrialized. The extent of discharge of domestic and industrial waste is such that rivers receiving untreated effluent cannot give dilution necessary for their survival as good quality water sources. The transfer of unfavorable releases from industries is detrimental to human and animal health and safety. [6] There is thus a challenge of providing water in adequate quantity and of the required quality to minimize hazards to human health and conserve the water bodies and the environment. Wastewater discharge from sewage and industries are major component of water pollution, contributing to oxygen demand and nutrient loading of the water bodies, promoting toxic algal blooms and leading to a destabilized aquatic ecosystem [12]

Evidence of the potential and observed human hazard due to environmentally acquired heavy metals and their ecological impact have been extensively studied, [13-16] The effects of industrial activities on the quality status of streams/rivers have been carried out by scholars in the past. Environmentalists and scholars in other disciplines have attempted to examine the impact of industrial activities on the physico-chemical parameters and heavy metal concentration of rivers/streams. Contaminated sediments do not always remain at the bottom of a water body. Anything that stirs up the water, such as dredging, can resuspend sediments. Resuspension may mean that all of the animals in the water, and not just the bottom-dwelling organisms, will be directly exposed to toxic contaminants. Different aquatic organisms often respond to external contamination in different ways, where the quantity and form of the element in water, sediment, or food will determine the degree of accumulation. The region of accumulation of heavy metals within fish varies with route of uptake, heavy metals, and species of fish concerned. Their potential use as biomonitors is therefore significant in the assessment of bioaccumulation and biomagnification of contaminants within the ecosystem.

2. Material and methods

Description of Study Area

The study area is Ikpoba River as shown in the map showing the different sampling locations.

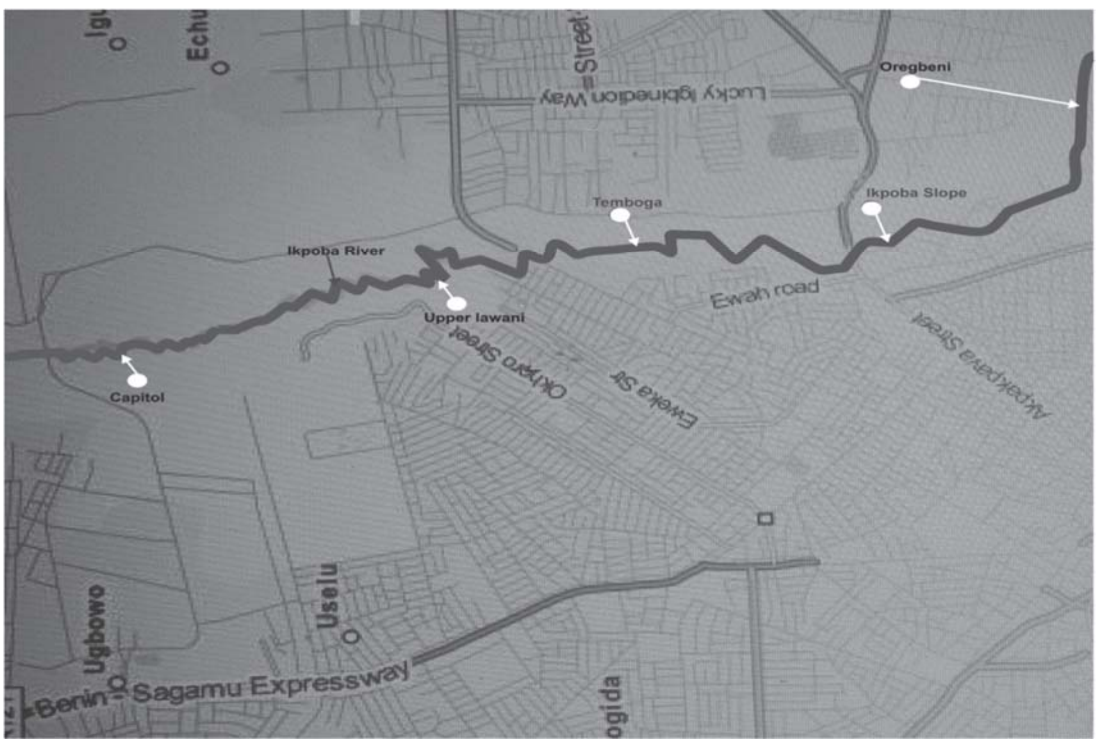

Fig 1: Map of Benin City showing Ikpoba River and the various sampling points.

Sampling and Sample Preparation

The water samples were collected using a one liter labeled polyethylene bottle which was previously treated with 5% nitric acid and rinsed with distilled water. The bottles were rinsed with the water to be sampled before the samples were collected. Triplicate water samples were collected at different points in a particular sampling location. The samples were preserved with 3ml of 1:1 Nitric acid per liter (Ademoroti, 1996) at the point of collection. Collected samples were transported to the laboratory in an ice chest were they were stored at 4 ^{0}C in a refrigerator. The sediment samples were collected using sediment grab and placed in labeled polyethylene bags which were previously treated with 5% nitric acid and rinsed with distilled water. The sediment samples were air dried in the laboratory for about 8 days prior to analysis. The fish samples were collected from commercial fish catch at the sampling location and were placed in labeled polyethylene bags. The fish samples were placed in an ice chest from the sampling point to the laboratory where they were dried at a temperature of about 101 – 105 ºC. The sediments sample was digested using Nitric acid, Perchloric acid and Sulphuric acid in the ratio of 1:2:2, in a fume cupboard. The fish samples were digested for heavy metal analysis using the same method described above. Heavy metal in the sediment and fish samples were determined with the aid of an atomic absorption spectrophotometer (AAS); Varian spectrAA 200 model.

Determination of Physicochemical Parameters of Water

The pH and electrical conductivity of the water samples was determined using a digital pH meter model GMBH D4040 NEUSSI and a conductivity meter; Radiometer Copen-Hagen CDM83. The total dissolved solids of the samples were determined using gravimetric procedure as described by Ademoroti (1996). sulphate content of the samples were evaluated using turbidimetric methods as stated by Ademoroti (1996). The chloride and nitrate values of the samples were determined using Mohr’s method APHA, (1993), and colorimetric method APHA, (1993) respectively. The phosphate content of the samples was evaluated using the ascorbic acid reduction method described by ASTM (1990). The heavy metals; Cd, Pb, Cr, Cu and Zn concentration of the water samples were determined with the aid of an atomic absorbance spectrophotometer (AAS)

3. Results and Discussion

Physicochemical Parameters of the water

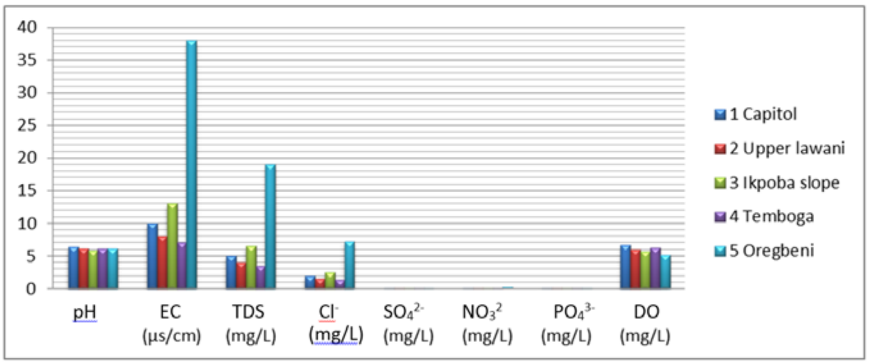

Fig 2: Shows the physicochemical parameters of the different sampling point

The pH value of water is an important indication of its quality and it is dependent on the carbon-dioxide carbonate–bicarbonate equilibrium. Acid base reactions are important in groundwater because of their influence on pH and the ion chemistry [5] The pH value in the study area varied between 5.78 and 6.40, with site 1 (capitol) having the highest value of 6.40 and site 3 (Ikpoba slope) having the lowest value of 5.78, low pH of water may be attributed to discharge of acidic water from agricultural and domestic activities. Site 3 is the receiving point of urban runoff. Mechanic workshops and commercial car wash are also common with this site. These activities may contribute to the low value of pH found in the site. Electrical conductivity ranges from 7-38 µs/cm. Electrical conductivity has it lowest value in site 4 (Temboga) and has it highest value in site 5 (Oregbeni), the high electrical conductivity in site 5 could be attributed to the discharge of inorganic materials including calcium, bicarbonate, nitrogen, phosphorus, iron, sulphur and other ions from the brewery close to the site into the water. Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulphate, and phosphate anions or sodium, magnesium, calcium, iron, and aluminum cations, [19]

TDS (Total Dissolve Solids) ranges from 3.5 – 19 mg/l, TDS also attain its lowest value in site 4 and highest value in site 5, the high TDS in site 5 could also be attributed to the discharge of organic and inorganic matters from the brewery to the water. Site 5 also has the highest value of 7.22, 0.24, 0.11 and 0.12mg/l for Chloride, Nitrate, Phosphate and Sulphate respectively compared to other sampling site which has relatively low value for the parameters above. The high value of Chloride, Nitrate, Phosphate and Sulphate in this site maybe due to the regular use of these compounds (Calcium Chloride, calcium phosphate, Nitrates which is present in chops, sulphates which is use to enhance better flavours) in the brewing process and the waste are thus discharge into the water body. DO (Dissolve Oxygen) values varied of from 5.1 – 6.6 mg/l, site 1 has the highest value of 6.6 mg/l and site 5 has the lowest value of 5.1 mg/l, the low value of DO in this site may be attributed to the high amount of oxygen use in the degradation of organic matter discharge into the water from the brewery and the pollution survey in Ikpoba river asserted that the low dissolved oxygen obtained for the effluent may be attributed to a high rate of oxidation stemming from the degradation of organic matter and thermal pollution from hot wash water and cooling water being discharged. [20] Most of the values obtained for the physiochemical parameters were within safe limit of USEPA, WHO and FEPA except for pH which was slightly lower than the USEPA standard of 6.5-8.5.

Heavy metal Concentration in Water

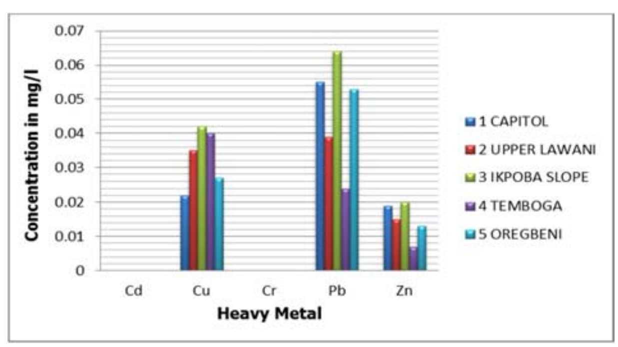

Fig 3: Shows the mean concentration of heavy metal mg/l of water in the different sampling site.

The heavy metal concentration at the different sampling point in Ikpoba river followed the order Pb>Cu>Zn>Cr=Cd, though the concentration of the metal depends on the extent of pollution in the sampling site. The mean concentration of lead ranged from 0.024±0.004 to 0.064±0.007mg/l. Lead attained it minimum value in site 4 (Temboga) and it maximum value in site 3 (Ikpoba Slope), the high concentration of lead in site 3 could be attributed to the high traffic density in the sampling site, the site is also a receiving point of agricultural and municipal waste. A similar study was also conducted [21] who reported that higher levels of lead often occur in water bodies near highways and large cities due to high gasoline combustion. Hardman *et al*. [22] reported that dust hold a huge amount of lead from the combustion of gasoline in automobile cars and these dust are washed to the nearby stream, Obasohan *et al* [23] also reported a high value of lead for this same river. copper concentration ranged from 0.022±0.002 to 0.042±0.002 mg/l, copper has it highest concentration in site 3 and the lowest concentration in site 1 (Capitol) the presence of copper in the sampling site could be attributed to the deposition of copper containing material in or around the river which are washed to the river, and tends to bio accumulate over time. The concentration of Zinc ranged from 0.007±0.002 to 0.020±0.002mg/l, zinc has maximum value in site 3 and it minimum value in site 4. Cadmium and Chromium were below detection limit of the equipment used, however Cadmium is a toxic metal and has no metabolic benefits to human and aquatic biota. Its presence in the aquatic ecosystem indicates contamination. From the analysis it can be seen that the concentration of heavy metal in the different sampling site in Ikpoba River has the maximum value in site 3, this could be drawn from the fact that site 3 been an area of activities that could lead to the production of these toxic metal which are directly or indirectly channeled to the river. Oguzie and Okhagbuzo [24] measured the Concentrations of heavy metals in effluent discharge downstream of Ikpoba River and then asserted that Ikpoba slope being the largest source of wastes from the city centre contains relatively high concentrations of the metals. This station and adjourning areas is the leading centre from where municipal, industrial and domestic wastes are generated and dumped indiscriminately by the inhabitants. The area is the leading centre for trade and mini-factory activities that generate wastes rich in heavy metals from duplicating and printing houses, gasoline servicing stations, poultry houses, market wastes, paints and dyes for clothing items and fumes from high vehicular traffic. According to Yong *et al*., (1992), heterogeneous masses from municipal, industrial and domestic throwaways were implicated as sources of metal pollutants in the aquatic environment. [25] reported relatively high levels of cadmium, lead and copper in effluents discharged into Ikpoba River during the rainy season. Similar reports on these metals were also documented for the same river by Obasohan and Oronsaye [26] Oguzie and Okhagbuzo [24] also brought to book that the effects of flood water in Benin metropolis after heavy rains is often devastating, as runoff water often transports loads of soil containing wastes through open drains and road surfaces from the City to Ikpoba river. Leachates from garbage and solid wastes often find their way into the river through underground drainage and surface flood run-off during the rainy season. However, most of the heavy metals determined for water were within the maximum permissible limit of WHO and NIS except for lead which was above the maximum permissible limit of 0.01mg/l of WHO and NIS standard.

Heavy Metal in Sediment

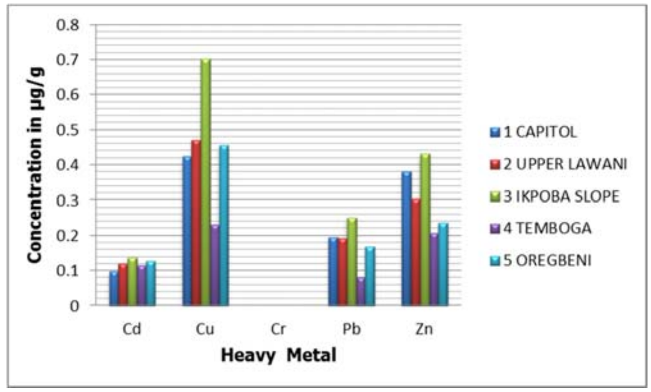

Fig 4: Shows the mean concentration of heavy metal in µg/g of sediment in the different sampling site.

Heavy metal in sediment in the different sampling site followed the order, Cu>Zn>Pb>Cd>Cr. The mean concentration of heavy metal ranged from 0.233±0.060 to 0.704±0.0162µg/g, 0.207±0.016 to 0.432±0.041µg/g, 0.081±0.029 to 0.252±0.027µg/g and 0.098±0.004 to 0.138±0.037µg/g for Copper, Zinc, Lead and Cadmium respectively. Chromium was below detection limit of the equipment used for the analysis. The result for the heavy metal analysis in sediment of Ikpoba River shows that the heavy metal in sediment were relatively high when compared to that of water. Ahmet., *et al.*, [27] Samir and Ibrahim, [28] Ogendi *et al*., [29] also recorded a higher value of heavy metal in sediment compared to the value obtained in water. This high level of heavy metal in the sediment is attributed to the fact that sediment is the sink of heavy metal which enters the water body from runoffs during the raining season. This runoff is known to contain heavy metals. The high concentration of heavy metal in site 3 (fig. 4) can be attributed to the fact that site 3 is closer to the pollution source. The higher concentration of heavy metal in the sediment shows that the sediment is the ultimate recipient of heavy metal in the aquatic ecosystem. However the concentrations of heavy metal obtained for the sediment were below the WHO maximum permissible limit for sediments

Heavy Metal in Fish

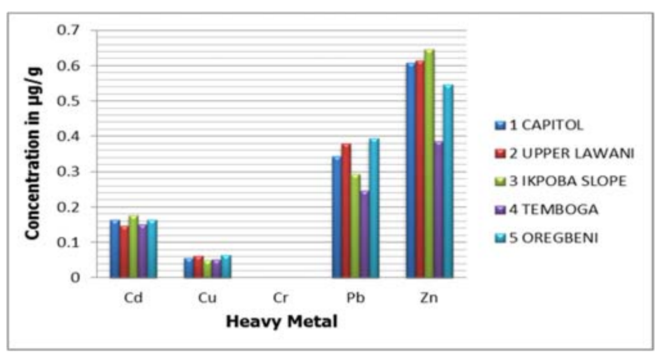

Fig 5: Shows the mean concentration of heavy metal in µg/g of fish in the different sampling location.

The concentration of heavy metal in fish followed the order Zn>Pb>Cd>Cu>Cr, the mean concentration of heavy metal ranged from 0.387±0.014 to 0.646±0.0079µg/g, 0.247±0.057

to 0.394±0.074μg/g, 0.148±0.009 to 0.176±0.006μg/g and 0.049±0.007 to 0.065±0.008μg/g for zinc, Lead, Cadmium and Copper. Chromium was bellow detection limit of the equipment used for the heavy metal analysis. The presence of these metals in the body part of fish serves as an indicator for the extent of heavy metal pollution of the water body from where these fish samples were obtained. This agrees with the report of the level of heavy metal in aquatic organism from different water bodies, the report showed that aquatic animal bio-accumulate heavy metals in considerable amount and because this metals are not bio-degradable the metals tends to stay in the tissue for a very long time.[30, 31] From this study the heavy metals result obtained for the fish were higher than that obtained in the water, this agrees with the concept that concentrations of heavy metals in fish tissues are always higher than that of water. [32] The high concentration of heavy metal in the sediment could also attribute to the high concentration of heavy metal in the fish, as fishes feed on benthic organism which has been contaminated by heavy metal from feeding in the bottom sediment. This also agrees with the report that Some contaminants in the sediment are taken up by benthic organisms in a process called bioaccumulation, When larger animals feed on these contaminated organisms, the toxins are taken into their bodies, moving up the food chain in increasing concentrations in a process known as biomagnification. As a result, fish and shellfish, waterfowl, and freshwater and marine mammals may accumulate hazardous concentrations of toxic chemicals (Abida *et al.* [5] However the maximum concentration of 0.646±0.079μg/g, 0.176±0.006μg/g and 0.065±0.008μg/g obtained for zinc, cadmium and copper respectively were within the maximum allowable limits of FOA and WHO standards for fish food. The maximum concentration of 0.394±0.0.074μg/g for lead exceeded the maximum permissible limit of 0.3μg/g of FOA for fish.

4. Conclusion

The study shows that sediment is the ultimate sink for heavy metal in the aquatic environment and these heavy metal concentration in the sediment tend to increase over time and thus leads to bioaccumulation of the metal in the aquatic organism. The study also shows that the higher the heavy metal concentration in the sediment, the higher the tendency of the heavy metal to bio-accumulate in aquatic organism. It was found that most of the heavy metal concentration of the water and fish samples were within safe limit except lead which exceeded the maximum permissible limit for water and fish.

The study recommends the need for constant monitoring of heavy metal concentration in Ikpoba River as it serve as a source of fish, agricultural and aesthetic activities in the area.

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