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Spatial trend in the heavy Metal Concentration of Ikpa River, Akwa Ibom state, Nigeria

Akpan AW[1], Ayotunde EO[2*], Etteokon SE[3]
[1, 3] Department of Animal and Environmental Biology, University of Uyo, Akwa Ibom State, Nigeria
[2] Department of Fisheries and Aquatic Science, Cross River State University of Technology, Calabar, Cross River State, Nigeria

Abstract
Studies on the Spatial Trend in the Heavy Metal Concentration of Ikpa River, Akwa Ibom State, Nigeria was undertaken in Ikpa River for a period of nine months (June, 2014 to February 2015). Triplicate water and sediment samples were taken monthly from four studied stations and were determined following standard methods. The result shows that the following heavy metals: Lead (Pb), Copper (Cu), Nickel (Ni), Iron (Fe), Chromium (Cr), Cadmium (Cd), Zinc (Zn), Manganese (Mn), Cobalt (Co) measured in water and sediment were above the acceptable limit of Federal Environmental Protection Agency (FEPA) apart from Vanadium (V), which was below the detectable limit. Sediment recorded higher concentration of heavy metals over water at the different study stations. The order of pollution according stations is as station 3 > stations 2 > 4. This shows that Station 3 was more polluted of heavy metals in water than other Stations with the higher concentrations of Cd, Pb, Cr, Cu and Co. In all the heavy metals examined in sediment, only Pb showed significant difference ($P<0.05$) across the Stations. The results obtained in this research were greatly influenced spatially due to various anthropogenic activities in the different study locations and shows that most of the heavy metals measured were above the recommended limit for tropical Rivers which indicate that Ikpa River is polluted of heavy metals especially in station 3. This however places aquatic organisms at great risk of survival as well as posing health challenge to human beings. Therefore, effort should be made at restoring and in the proper management of the river to save this aquatic ecosystem.

Keywords: heavy metal, Ikpa River, spatial trend, Akwa Ibom state

1. Introduction
Water is one of the most essential and abundant compounds of the ecosystem as all living organisms on earth including humans require water for their survival and growth. Unfortunately, the availability and quality of water have been impacted upon by both natural and anthropogenic sources due to increased human population, industrialization, use of fertilizers in agriculture which have all contributed to the different harmful contaminants in the aquatic ecosystem leading to the poor water quality and productivity of aquatic ecosystems (FAO, 1993) [7].

Heavy metals are among the contaminants that affect the inherent quality of most of Rivers including Ikpa River. Heavy metals are categorized as metallic elements with relatively high atomic weight and highly toxic even at low concentration, they are the natural constituents of the earth crust which cannot be degraded (Butu and Iguisi, 2013) [3]. Aquatic environment naturally contain little amounts of heavy metals since trace amount of some heavy metals are needed by living organisms for their various metabolic processes (Butu and Iguisi, 2013) [3]. Anthropogenic source of heavy metals pollution could result from industrial wastes, ore mining and processing activities, smelting plants, rolling mills plants for the surface treatment of metals, film, textile and leather industries, petroleum exploration, industrial effluents and agro-chemical application in the environment. It could also result from natural means such as acidic rains, earthquake, landslides, cyclones and tornadoes (FAO, 1993, Oze *et al.*, 2005; Butu and Iguisi, 2013) [7, 14, 3]. Atmospheric precipitation can wash out metal in dust and aerosols generated by the burning of fossil fuels by the exhaust gases of motor vehicles and from other sources (Mackie, 1998) [12].

The presence of heavy metals in aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behaviour (Heath, 1995; Saghali *et al.*, 2014) [8, 16]. The metals found to be of highest importance to fisheries include Aluminium, chromium, iron, nickel, copper, zinc, arsenic, cadmium, mercury and lead (FAO, 1993) [7]. These metals usually produced toxic effects particularly bioaccumulation.

The rate of bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to digest the metals and the concentration of such metal in the River. Also it has to do with the concentration of the heavy metal in the surrounding soil sediments as well as the feeding habits of the organisms (FAO, 1993) [7]. Aquatic animals (including fish) bioaccumulate trace metals in considerable amounts and stay over a long period. Fishes have been recognized as a good accumulator of organic and inorganic pollutants (King and Jonathan, 2003) [10]. The increasing levels of environmental pollutions by toxic metals from various sources have generated a great concern on the impact on human health (Ogar *et al.*, 2013) [13]. A large amount of those metals taken in by plants and animals subsequently find their way into the food chain. This ever increasing pollution has given rise to concern on the intake of harmful metals in humans. Humans are prone to different routes of exposure (Ogar *et al.*., 2013) [13].

With these effects, monitoring of the quality of water becomes imperative as it permits direct assessment of the Rivers that are exposed to deleterious anthropogenic factors. Although studies on heavy metals have been carried out in Southern Rivers, much have not been done in Ikpa River and hence this research, this study will cover the whole length of

the River in order to have the baseline on changes caused by natural and anthropogenic processes as this will provide an update information on the level of some heavy metal concentrations in Ikpa River which will help in policy formulations for the proper management of the River.

2. Materials and Methods

2.1 Study Area

Ikpa River is situated in Akwa Ibom State (Latitude 05º11′ N and 05º16′N and Longitude E07º55′E and 08º07′E) within the rainforest zone of Southeastern Nigeria (Fig. 3.1). It is a small perennial rainforest River located west of the lower reaches of the Cross River System. It drains a catchment area of 516.5km^2, 76.5km^2 (14.8%) of which is liable to annual flooding. The total length of the main channel (between its source in Ikono and discharge point into the Cross River Creek close to Nwaniba in Uruan L.G.A) is 53.5km. The Cross River finally empties into the Atlantic Ocean. The River drains several parts of Akwa Ibom State including Ikono, Ibiono Ibom, Itu, Uyo and Uruan Local Government Areas of Akwa Ibom State.

The climate of Ikpa River is typical of tropical rainforests, comprising of two main seasons: the wet and the dry season. The wet season is characterized by heavy rains and thunderstorms that last from April to October, while the dry season covers the months of November to March. The monthly distribution of rainfall shows a noticeable fluctuation in the month of August usually termed as the "August break". The mean annual rainfall varies from 2250mm to about 1500mm during the wet and dry seasons. The average minimum and maximum temperature are about 25 ºC and 32 ºC respectively. The wet season is also characterized throughout the area by relatively low temperatures and a high relative humidity (85 - 95%). The dry season is marked by the dry harmattan winds whose intensity is more felt from late November to early January. The mean annual potential evapo-transpiration (PET) varies from 1425 to 1625mm (Ekpo, 2013) [5].

2.2 Location of Sampling Stations

Four sampling Stations (1 - 4) were chosen along the River course based on the anthropogenic impact in these Stations. The co-ordinates of the sampling stations were taken using Geographic Positioning System (GPS). Station 1, Edem Iyire is the source of the River (Upstream) located latitude: N007º49'47.6" and longitude: E05º09' 25.0". It is a small headwater stream which is shaded by riparian vegetation. The topography of the catchment is hilly and elevated. The river is fast flowing which may be due to land excavation and dredging activities carried out in the area. The River serves as a source of drinking water for the rural community. Laundry activities are also carried out in the River.

Stations 2 is Ntak Inyang (Midstream) located centrally along the Calabar-Itu highway. It lies Latitude: N007º53'59.2" and Longitude: E05º05'04.5". The Station is characterized by moderately fast water current. The bottom of the River is prominently sandy and muddy. The topography of the catchments is characterized by gentle slope. Some parts of this water surface are covered with floating leaves of *Azolla* and *Salvinia* species. The riparian zone is dominated by strands of *Raphia hookeri* and *Raphia vinifera.* Sand dredging and fishing are carried out in this Station.

Station 3 (Iba Oku) is also located centrally (midstream) along Uyo Village road and lies within Latitude: N007º56'11.9" and Longitude: E05º04'10.3". The River is marked with a reduced flow current with a sloppy topography of the catchment attributed to the gully erosion in this area. The erosion site of the University of Uyo, town campus drains into this station while Uyo urban waste usually dumped at the ravine along Eka Street (Uyo) also drains into this tributary. Bathing, laundry and refuse dumping are carried out along the bank.

The lower Ikpa River, Station 4 (Nwaniba) is the downstream segment that discharges into Cross River Creek. It is located within Latitude N008º01'15.2" and Longitude: E05º03'25.7"; is tidal and shaded by overhanging canopy of riparian vegetation mostly *Elaeis quineensis, Pandanus candelabrum, Raphia hookeri, R. vinifera* and other tropical forest trees. The predominant aquatic macrophytes are *Nymphae*, *Vossia*, *Utricularia* and *Musanga crinium.* Human activities in the area include fishing, farming, boat building and wood logging.

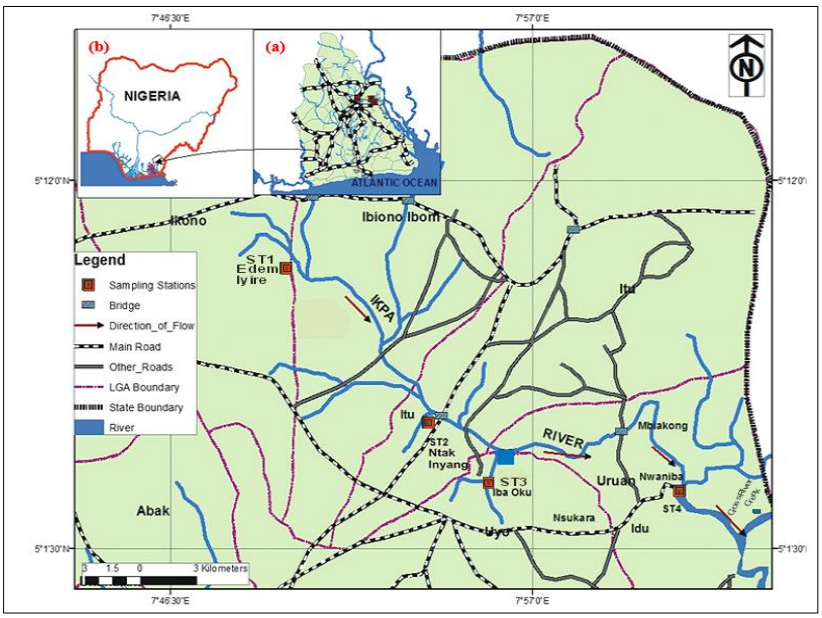

Fig 1: Location of the Study Stations in Ikpa River Basin. Inset: **(a)** Location of Ikpa River on the Map of Akwa Ibom State. **(b)** Location of Akwa Ibom State on the Map of Nigeria

2.3 Samples Collection

Water and sediments samples were collected once a month between the hours of 9am – 12pm for a period of nine months in the four sampling Stations; Edem Iyire (1), Ntak Inyang (2), Iba Oku (3) and Nwaniba (4). Water was taken in each of the Stations at a depth of 30cm below the surface using one litre plastic containers with screw caps tightly covered to avoid trapping of air. The container was initially rinsed with concentrated HNO_3 and later rinsed with distilled deionized water.

2.4 Heavy Metal Analysis of Samples

The following heavy metals: Lead (Pb), Copper (Cu), Nickel (Ni), Iron (Fe), Chromium (Cr), Cadmium (Cd), Zinc (Zn), Vanadium (V), Manganese (Mn), Cobalt (Co) in water were all determined following standard methods (APHA, 2005). In the analysis of heavy metals in the sediment, 5g of the sediment samples in each of the Stations were air dried for an hour and thereafter oven dried to a constant weight at $105^0{}_C$ for an hour. The samples were grounded using clean agate mortar and pestle and sieved through 2mm mesh size to remove coarse materials. A quantity of 5g of sediment in each of the stations was digested using 0.2m Hydrochloric acid (HCl) and Nitric acid ($HNO_{3)}$ in the ratio 1:3 in a fume cupboard at 80ºC until fumes become white. The liquid was cooled and transferred into 100ml volumetric flask and made up to the mark with distilled water. Heavy metal concentrations were detected by atomic absorption spectrophotometer (AAS) Hitachi model 180-70 polarised zeaman.

3. Result and Discussion

Mean concentration of heavy metal in water and sediment samples in the four studied stations are presented in Table 1 and 2 respectively with the national guidelines for water qualities permissible limit for various uses in Nigeria as provided by FEPA for comparison.

Table 1: Spatial Variation in the Heavy Metal Concentrations in Water of Ikpa River

	Station 1		Station 2		Station 3		Station 4		FEPA
Parameters	**Mean**	**±SE**	**Mean**	**±SE**	**Mean**	**±SE**	**Mean**	**±SE**	
Cu (mg/l)	0.606[a]	0.049	0.624[a]	0.109	0.692[a]	0.271	1.216[a]	0.385	1.00
Zn (mg/l)	6.714[a]	0.450	7.460[b]	0.716	6.928[a]	0.843	7.5[a]	0.833	3.00
Fe (mg/l)	2.15[a]	0.670	2.832[a]	0.568	3.078[b]	0.806	3.444[b]	1.115	0.30
Ni (mg/l)	0.60[a]	0.116	0.761[a]	0.115	0.813[a]	0.269	1.113[a]	0.282	0.02
Cd (mg/l)	0.324[a]	0.045	0.345[a]	0.150	0.730[a]	0.395	0.535[a]	0.316	0.03
Mn (mg/l)	0.869[a]	0.160	0.978[a]	0.161	1.739[b]	0.411	1.611[a]	0.159	0.2
Co (mg/l)	0.043[a]	0.019	0.060[a]	0.029	0.101[a]	0.150	0.106[a]	0.086	0.02
Pb (mg/l)	0.154[a]	0.058	0.441[a]	0.295	1.131[b]	0.989	0.757[a]	0.005	0.01
Cr (mg/l)	0.004[a]	0.007	0.025[a]	0.002	0.063[a]	0.059	0.063[a]	0.059	0.05
V (mg/l)	0.001[a]	0.000	0.002[a]	0.001	0.003[a]	0.002	0.003[a]	0.002	NG

*Similar letters superscript indicates means that are not significantly different (P<0.05) and vice versa
SE: Standard Error. NG: No Guideline. FEPA: Federal Environmental Protection Agency.

Table 2: Spatial Variation in the Heavy Metal Concentrations in sediment of Ikpa River

	Station 1		Station 2		Station 3		Station 4		FEPA
Parameters	**Mean**	**±SE**	**Mean**	**±SE**	**Mean**	**±SE**	**Mean**	**±SE**	
Cu(mg/kg)	2.180[a]	0.158	2.299[a]	0.086	2.128a	0.289	2.320[a]	0.305	1.00
Zn (mg/kg)	10.97[a]	0.863	11.17[a]	1.830	9.383[a]	1.343	12.535[a]	2.821	3.00
Fe (mg/kg)	6.345[a]	2.252	6.229[a]	1.968	5.594[a]	2.051	6.357[a]	2.521	0.30
Ni (mg/kg)	1.794[a]	0.232	1.537[a]	0.170	1.537[a]	0.311	1.468[a]	0.228	0.02
Cd(mg/kg)	2.763[a]	0.263	3.169[a]	0.437	1.977[a]	0.480	1.668[a]	0.536	0.03
Mn(mg/kg)	0.531[a]	0.492	3.637[a]	0.840	2.553[a]	0.507	0.651[a]	0.436	0.2
Co(mg/kg)	0.409[a]	0.110	0.523[a]	0.047	0.483[a]	0.093	0.493[a]	0.113	0.02
Pb (mg/kg)	5.866[a]	0.481	0.117[b]	1.272	5.127[a]	1.229	2.612[b]	0.849	0.01
Cr (mg/kg)	0.432[a]	0.059	0.491[a]	0.008	0.406[a]	0.076	0.424[a]	0.068	0.05
V (mg/kg)	0.02[a]	0.000	0.02[a]	0.000	0.03[a]	0.009	0.018[a]	0.002	NG

*Similar letters superscript indicates means that are not significantly different (P<0.05) and vice versa
SE: Standard Error. NG: No Guideline. FEPA: Federal Environmental Protection Agency.

Copper (Cu) recorded the lowest (0.606 ± 0.049) mg/l and the highest mean values (1.216 ± 0.385) mg/l in Station 1 and 4 respectively with no significant difference (P < 0.05) across the Stations. In the sediment, its lowest mean concentration (2.128 ± 0.2899) was in Station 3 and the highest (2.320 ± 0.305) mg/kg in Station 4. Cu values were above the FEPA limit of 1.0 and were significant in all the Stations.

Zinc recorded a higher mean concentration (7.5 ± 0.833) in station 4 and a lower concentration (6.714 ± 0.450) in Station 1. In all the studied Stations, mean concentration of Zn was significantly different (P < 0.05, 7.460 ± 0.716) only in Station 2. The mean values of Zn were above the FEPA recommended limit (3.0) in all the Stations. In the sediment, Zinc also recorded its lowest mean concentration (9.383 ± 1.343)mg/kg in Station 3 and the highest in (12.53 ± 2.821)mg/kg in Station 4. The concentration of Zn did not show any significant difference (P <0.05) across the four Stations but were above the FEPA recommended limit (3.0) which were significant in all the Stations.

Mean values of Iron varied from (2.15 ± 0.670) in station 1 to (3.444 ± 1.115) in Station 4 with a significant difference between Stations 3 (P < 0.05, 3.078 ± 0.806)mg/l and 4 (P< 0.05, 3.444 ± 1.115)mg/l. However, the mean values of Fe were above the FEPA recommended limit (0.30) in all the Stations. In the sediment, Iron recorded the lowest (5.594 ± 2.051)mg/kg and highest mean concentration (6.357 ±

2.521)mg/kg in Station 3 and 4 respectively. No significant difference (P < 0.05) was recorded in the concentration of Fe in all the Stations.

Nickel varied in its mean concentration from (0.60 ± 0.116)mg/l in Station 1 to (1.113 ± 0.282)mg/l in Station 4. The mean concentration of Nickel in the sediment varied from (1.537 ± 0.170)mg/kg to (1.794 ± 0.232)mg/kg in Stations 2 and 1 respectively. Ni also showed no significant difference in its concentration across the studied Stations but was above the FEPA recommended limit (0.02).

A higher mean concentration (0.730 ± 0.395) of Cadmium was recorded in Station 3 and the lowest (0.324 ± 0.045) was in Station 1. There was no significant difference (P<0.05) in the mean values of Cd but they were slightly above the FEPA limit (0.003) in all the Stations. The lowest mean concentration (1.668 ± 0.536)mg/kg of Cadmium in the sediment was recorded in Station 4 and the highest (3.169 ± 0.437)mg/kg was in Station 2 with no significant difference across the Stations. The mean values of Cd in the sediment were above the FEPA limit (0.03) and this was significant in all the four Stations.

Manganese mean values ranged from the lowest (0.869 ± 0.160) mg/l in Station 1 to 1.739 ± 0.411) mg/l in Station 3 which was significantly (P < 0.05) higher than other Stations. With regards to the FEPA guideline (0.2), all the mean values of Mn in all the Stations were significant as they were above the recommended limit. Manganese which was not significantly different (P <0.05) across the Stations in the sediment ranged from (0.531 ± 0.492)mg/kg to (3.637± 0.840) mg/kg in Stations 1 and 2 respectively.

Cobalt ranged from (0.043 ± 0.019) to (0.106 ± 0.086) mg/l in Station 1 and 4 respectively with no significant difference across the four Stations. The lowest mean concentration (0.409 ±0.110)mg/kg of Cobalt in the sediment was obtained in Station 1 and the highest (0.523 ± 0.047)mg/kg was obtained in Station 2 with no significant difference (P< 0.05) across the Stations.

Lead varied from (0.154 ± 0.058) in Station 1 to (1.131 ± 0.989) in Station 3 which was significantly (P< 0.05) higher than other Stations. With regards to the FEPA guideline (3.0), all the mean values of Pb in all the Stations were significant as they were above the recommended limit. The lowest significant mean concentration (P <0.05, 0.117 ± 1.272) of lead in the sediment was obtained in Station 2 and the highest (5.866 ± 0.481)mg/kg was obtained in Station 3. A significant difference was recorded in the mean values of lead between Stations II and IV. The values obtained in Stations 2 (P< 0.05, 0.117 ± 1.272) and 4 (P < 0.05, 2.612 ± 0.849) were significantly lower than other two Stations. Generally, Pb mean values were above the FEPA limit of 0.01 and were significant between Stations.

The lowest mean value (0.004 ± 0.007) of Chromium was recorded in Station 1 and the highest (0.063 ± 0.059) mg/l in Stations 3 and 4 with no significant difference across the Stations. In the sediment, it varied from the least mean value (0.406 ± 0.076)mg/kg in Station 3 to the highest (0.491 ± 0.008) in Station 2 with no significant difference across the Stations.

In all the heavy metals examined in water across the four Stations in Ikpa River, Cu, Ni. Cd, Co and Cr were not significantly different (P <0.05) and were within the FEPA recommended limit apart from Cd which was slightly above the limit of 0.003. In the sediment, there was no significant difference across the stations in all the parameters apart from Lead in which Stations 1 and 3 were similar with a higher mean concentration over Stations 2 and 4 but Station 2 was significantly lower (P<0.05) than all other Stations while Station 4 was significantly higher (P<0.05) than Station 2 and lower than Stations 1 and 3. All the heavy metals examined in the sediment were above the FEPA recommended limit apart from Vanadium which was below the detectable limit.

The result of the study shows that the concentration of heavy metals in the water varied across the Stations. These variations are mainly due to different sampling spots. Mean concentration of zinc was significantly higher (P<0.05) in Station 2 than other Stations. It was also above the FEPA limit of 3.0. This clearly shows that Station 2 was polluted of zinc and could be linked with the dredging activities as well as the usual loading of sands in tippers along the shores of the River as well as the location of this station along the highway since motor vehicle exhaust are capable of emitting hydrocarbons into the River which increases the load of heavy metals in addition to erosion and agricultural runoff (Williams and Feltmate, 1992; Ahmed, 2016) [20, 2]. The low concentration of Zinc recorded in sediment in Station 3 could be linked to the low activities of this Station compared to high activities Station 4 which recorded the high of concentration of Zinc. The high concentration of zinc recorded in Station 4 could be attributed to the high temperature with corresponding low dissolve oxygen recorded in Station 4 as Lawson (2011) [11], has reported that high temperature and low dissolved oxygen concentration lead to an increase in toxicity of Zinc. pH may have contributed greatly to the high concentration of Zinc in Station 4 as Ideriah *et al.* (2012) [9] have reported that heavy metals including Zinc get adsorbed onto the sediment surface at different pH. The concentrations of Zn measured could also be attributed to refuse dump, domestic sewage sources as well as dumping of decaying roofing sheets and metal components containing Zn in the sediment as Zn was observed to be the only roofing sheet used in most houses around this Station.

Fe was significantly higher (P<0.05) in Station 3 over other Stations. This was traced to the leaching from erosion site, refuse dump as well as its nearness to highway in addition to its shallow nature which tends to concentrate most of the environmental parameters washed and emitted into the River (Song *et al.*, 2015) [17]. The differences in the levels of Fe in sediment across the Stations were not significant (P>0.05) but were above the FEPA level of 0.30. This results indicate that Ikpa River especially Station IV which recorded the high concentration is highly contaminated with Fe. The geochemical and biochemical processes in the aquifers within the catchments according to Lawson (2011) [11] may be responsible for the observed differences.

Mean concentration of Mn in Stations 3 and 4 was significantly higher than other two Stations (1, 2). This was attributed to the location of these stations along the roads as well as agricultural runoff from the catchment into the River. According to Ahmed *et al.* (2016) [2], increase in the use of metal based fertilizers in agricultural revolution could result in the continued rises in the concentrations of metal pollutants in freshwater due to water runoff. In the sediment, Stations 2 and 3 recorded the highest concentrations of Mn compared to Stations 1 and 4. This was attributed to the refuse dumps, run-off input into Stations 2 and 3 which result in the high rate of microbial decomposition causing oxygen depletion. According to Lawson (2011) [11], manganese occurs in sediment that is low in oxygen.

Lead was significantly higher (P<0.05) in Station 3 over other Stations. This higher concentration in low activity Stations 3 over other Stations was traced to urban runoff and location of Station 3 closed to the road which according to Williams and Feltmate (1992) [20], urban runoff contains significant quantities of lead related to the proportion of catchment area allotted to motor vehicles and the density of traffic. The high concentration of lead in Station 3 signifies that emissions from automobile which frequently ply along the River in Uyo village road either to Calabar Itu highway or to Wellington Bassey way where government house and Uyo L.G.A. headquarters among others are located or to other neighbouring communities were the major sources of Lead in the area. In the sediment, a significant lower mean concentration (P<0.05) of Pb was obtained in Stations II and IV while insignificant higher mean concentration were recorded in Stations I and II. The concentration of Pb in all the Stations was higher in sediment than in water. The higher concentrations of Lead measured in sediment than in water indicate that lower pH favoured metal accumulation and is in agreement with report that sediments are the major depository of metals holding more than 99% of total amount of a metal present in the aquatic system (Ideriah, 2012) [9] This is also in line with WHO (2008) [19] report that Pb largely accumulates in bottom sediments at concentrations about four orders of magnitude greater than in the water.

Other heavy metals such as Copper, Cadmium, Chromium and Cobalt were not significantly different among the studied Stations in the water. However, Copper recorded a higher concentration in Station 4 which exceeded the FEPA limit over other stations and this could be traced to the catchment farming as well as the dumping of waste in the station. Uqwu *et al.* (2008) reported that the occurrence of metal contaminants in Nigerian Rivers in excess of the natural levels was as a result of growth in human population, sophisticated industries and modern practices coupled with lack of environmental regulations. The concentration of Cu in the sediment was higher Downstream in the high activities Station 4 than the Midstream Station 3 with low activities. A higher concentration of Copper in Stations 2 and 4 in the sediment implies that these stations were contaminated with copper resulting from dredging and harbour activities along the shoreline. In addition emissions from outboard engines, may have contributed to the levels of Cu measured in these Stations.

Cadmium concentration in water was higher in Station 4 over other Stations and exceeded the FEPA limit. The concentrations of cadmium in the sediment also increased in the midstream Stations 2 and decreased in the downstream Station 4 due to the corresponding decrease in the sources of Cadmium pollutant downstream. The high concentrations of Cd recorded midstream was contributed by weathering of minerals and soils, abandoned metals parts during timber processing, discharge of domestic effluents and urban storm-water runoff containing Cd-laden materials (Lawson, 2011) [11].

Chromium concentrations in water were within the FEPA range across the Stations but in Stations 3 and 4 the concentration were higher than the other two Stations (1 and 2). Generally, the concentration of Chromium in the sediment was low with no significant difference (P<0.5) in all the studied Stations, but slightly higher concentrations was recorded in Station 2 over other Stations and were mainly contributed by deposits of abandoned metals parts due to the dredging activities, boat repairs in addition to the emission of hydrocarbon leaked from vehicle plying the road along the Station which serve as a source of heavy metals in water (Williams and Feltmate 1992; Ahmed *et al.*, 2016) [20, 2].

Cobalt mean concentrations in Stations 3 and 4 were higher than in Stations 1 and 2. In the sediment, the concentrations of cobalt though not significant (P<0.5) across the stations recorded slight higher concentrations in Stations 2, 3 and 4 than in Station 1. The location of these Stations along the highways may be the possible source of cobalt into the River due to hydrocarbon emissions from auto-mobile plying these roads (Williams and Feltmate 1992; Lawson, 2011; Ahmed *et al.*, 2016) [20, 11, 2].

Nickel recorded a higher concentration which exceeded the FEPA limit of 0.02 in Station 4 over other Stations while in the sediment, the concentrations increased in the upstream and midstream (Stations 1 and 2) and decreased downstream. This was attributed to the fact that the Nickel inducing factors were decreasing progressively downstream. The high concentrations upstream according to Ideriah *et al.* (2012) [9] was linked to the topography of the studied area, leaching and run off of rain water which drains automobile emissions that settled into the sediment of the River.

In all the Stations studied, Station 3 recorded a significant higher concentration in the heavy metals of Fe, Mn and Pb while Stations 2 and 4 recorded a significant (P<0.05) higher concentration in Zn and Fe respectively. No significant difference was recorded in Station 1 in all the parameters examined. This shows that Station 3 was more polluted of heavy metals in water than other Stations with the higher concentrations of Cd, Pb, Cr, Cu and Co. A significant higher concentration of Cd, Pb, Cr, Cu and Co in Station 3 Could have been due to the lower volume of water (shallow) and width of Station 3 which influenced the high concentrations of some metal measured at this low activity Station 3. Also, refuse dumping including plumbing materials, which are high in lead compounds; agricultural discharge from the catchment; leaching of laterite soil from the university of Uyo town campus erosion site into Station 3, accounted for the oxygen depletion thereby encouraging high concentrations of heavy metals.

Depletion of dissolve oxygen in water supplies can encourage microbial reduction of nitrate to nitrite and sulphate to sulphide, giving rise to odour problems as well as increase in the concentration of iron II in solution (Adakole *et al.*, 2008) [1]. This can affect the abundance and distribution of biological organisms according to Ezeonyejiku and Obiakor (2013) [6] who reported that metals and other pollutants such as sewage, sawdust, hydrocarbons and organic wastes, when introduced into water bodies can bring about alteration of physical characteristics of such a water body and hence would affect species diversity. The presence of heavy metals in aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behaviour (Heath, 1995; Ogar *et al.*, 2013; Song *et al.*, 2015) [8, 13, 17]. Heavy metals contamination of fresh water may have a devastating effect on the ecological balance of the recipient environment and a diversity of aquatic organisms (Ogar *et al.*, 2013) [13]. According to Ogar *et al.* (2013) [13], metals such as Cd, Pb, and Hg have no known essential role in the body of aquatic organisms and are toxic even at low concentrations.

Almost all the heavy metals measured in water apart from vanadium (V) which was below the detectable level exceeded the FEPA limit for drinking water in most Stations.

Generally, a higher concentration of heavy metals in the sediment at the different study stations in Ikpa River over water may be due to discharge of household, light industrial, palm oil agriculture, road side run offs and other anthropogenic related activities located within the River or in close proximity to these study locations. Metals entering into the River through natural processes such as weathering, erosion and dissolution of water-soluble salts constitute the background level, but those added through anthropogenic activities substantially enhance the concentrations in sediment (Rzeetala, 2015; Ahmed *et al.*, 2016) [15, 2]. It may also result from precipitation of heavy metals from the water column under slightly elevated pH conditions and from the absorption of heavy metals into organic matter and their settlement downwards (Begun, 2009; Eddy, 2014; Ahmed *et al.*, 2016) [4, 2]. The higher concentration of heavy metals in sediment over water recorded in this study agrees with the work of Saghali (2014) [16] who observed that, sediment accumulate high volumes of contaminants compared to the water column. Sediment is the ultimately depository of many chemical compounds including heavy metals from natural and anthropogenic sources which places biological organisms such as benthos at risk of contamination compared to pelagic organisms (Saghali *et al.*, 2014; Rzeetala, 2015) [15, 16]. As stated by Ogar *et al.* (2013) [13], heavy metals contamination may have a devastating effect on the ecological balance of the recipient environment and a diversity of aquatic organisms.

In all the heavy metals examined in sediment, only Pb showed significant difference ($P<0.05$) across the Stations while others were not significantly different.

4. Conclusion

The result of the study across the Stations depict that, Station 3 was more impacted with a significant higher concentration in the heavy metals of Fe, Mn and Pb while Stations 2 and 4 recorded a significant ($P<0.05$) higher concentration in Zn and Fe respectively. No significant difference was recorded in Station 1 in all the parameters examined. This shows that Station 3 was more polluted of heavy metals in water than other Stations with the higher concentrations of Cd, Pb, Cr, Cu and Co. All the heavy metals measured in water apart from vanadium (V) which was below the detectable level exceeded the FEPA limit in most Stations. In the study, a higher concentration of heavy metals was recorded in the sediment over water at the different study stations in Ikpa River. In all the heavy metals examined in sediment, only Pb showed significant difference ($P<0.05$) across the Stations.

The results obtained from this research also shows that most of the heavy metals measured were above the recommended limit for tropical Rivers while few were in conformity with the recommended limits. The results were greatly influenced spatially due to various anthropogenic activities in the different study locations. These anthropogenic activities have greatly affected the diversity of biological species due to the stress imposed on these organisms in the River. It also renders the water unsafe for drinking for the rural populace which relies on river as a source of drinking water. Therefore, effort should be made at restoring and in the proper management of the river to save this aquatic ecosystem.

5. References

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