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RESEARCH ARTICLE

Evaluation of Metal Contamination on the Surface Sediments of Akpa Yafe River, Bakassi, Cross River State, Nigeria

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Abstract

Evaluation of metal contamination on the surface sediments of Akpa Yafe River was carried out in four locations: location 1 (Ikang), location 2 (Esuokon), location 3 (Ifiang Ayong) and location 4 (Archibong). The sampling was carried out over a period of three months (August to October 2012) to determine the level of accumulation of metals in the river sediment in view of effective utilization, better management, conservation and sustainable exploitation of the river resources. The concentrations of eight metals (Hg, Co, Mn, Cd, Ni, Fe, Pb and Zn) were determined. Nickel (Ni) had the highest concentration values with range of 0.232-0.521 mg/kg and mean value of 0.311 mg/kg followed by iron (Fe) with range of 0.117-0.414 mg/kg and mean value of 0.195 mg/kg. Mercury (Hg) was found only in one location and had the least concentration (0.004 mg/kg). The systematic sampling of the river bed sediments at predefined locations revealed that the metal accumulation is very close to normal but slightly beyond threshold limits. There is a need to control municipal wastes constantly discharged into Akpa Yafe River to avoid any negative impact of pollution.

Keywords: Metal contamination, sediments, Akpa Yafe River, nickel, municipal wastes, pollution.

Introduction

Sediment is the loose sand, silt and other soil particles that settle at the bottom of the body of water (USEPA, 2002). It can come from soil erosion or from decomposition of plants and animals. Wind, water and ice help to carry these particles to rivers, lakes and streams. Sediments can be sensitive indicators for monitoring contaminants in an aquatic environment. They are said to be polluted with various kinds of hazardous and toxic substances including metals which accumulate in sediment via several pathways including disposal of liquid effluents, terrestrial runoff and leachates carrying chemicals originating from numerous urban, industrial and agricultural activities as well as atmospheric deposition. All these important factors and more modify water and sediment compositions, thus affecting the benthic and other aquatic organisms. Sediments have provided useful information on the changes of the river and also contain information that occurred in pre-cultural time in the river and its catchment areas. Human activities play a major role in the introduction of various anthropogenic pollutants in surface waters. Among the pollutants are metals which at high concentration become toxic. Moreover, metals can be absorbed from the water column into fine particle surface and later reside more towards sediment matrices. Metals also participate in various biogeochemical processes, have significant mobility and can affect the ecosystem through bioaccumulation and biomagnification processes and are potentially toxic for environment and for human life (Manahan, 2000; Ahmed and Al-Hajri, 2009; Gaur and Dhankhar, 2009; Abdul Aziz *et al.,* 2010; Hasan *et al.,* 2010). As a combined result of these factors, metal concentration in sediment change with space and time. In fact, during the last few decades, industrial and urban activities have contributed to the increase of metal contamination into aquatic environment and have directly influenced the coastal ecosystem.

Various studies have demonstrated that aquatic sediments are contaminated by heavy metals from industrialized coastal areas; therefore, the evaluation of metal distribution in surface sediment is useful to assess pollution in the aquatic environment (Solomon and Forstner, 1984; Zonta *et al.,* 1994; Bellucci *et al.,* 2002). Different studies have widely confirmed the serious contamination of river sediments by heavy metals (Priju and Narayana, 2007; Mumba *et al.,* 2008; Kashulin *et al.,* 2008; Mensi *et al.,* 2008; Akoto *et al.,* 2008; Venugopal *et al.,* 2009; Oygard and Cyengedal, 2009; Nouri *et al.,* 2010). The sediment history broadly reflects the contamination history of an area. Environmental pollution due to urbanization, agriculture and industrial development is a major concern. Further studies have been conducted to evaluate the distribution and speciation of heavy metals in sediment (Karbassi *et al.,* 2007; Cuculic *et al.,* 2009). Sediment analysis is increasingly important in evaluating qualities of a body of water.

Fig. 1. Map showing sampling locations.

In addition to the water sample analysis, practiced for years in comparison to water testing, sediment testing reflects the long-term quality situation independent of current input (Hodson, 1986; Haslam, 1990). The purpose of this study is to determine the heavy metal thresholds in Akpa Yafe River sediments with an aim of providing baseline data for further investigations of the pollution status of the river.

Materials and methods

Study area: Akpa Yafe River lies approximately between latitude 4.683^{o}N and longitude 8.517^{o}E. It is a tributary of Cross River and forms a natural boundary between Nigeria and Cameroon by the Eastern flanks of Akpabuyo/Bakassi Local Government Areas of Cross River State. The river basin covers an area of 54,000 km^3 with 14,000 km^3 in the Cameroon and 40,000 km^3 in Southern Nigeria. It takes its rise from the Atlantic Ocean.

Sampling locations: Four sampling stations were identified during the study period. The sampling stations were: station 1(Ikang), station 2 (Esuokon), station 3 (Ifiang Ayong) and station 4 (Archibong) respectively (Fig. 1). Human activities here include small scale farming, trading and artisanal fisheries. The total distance from station 1 to station 4 is 23.01 km. The distance from station 1 to station 2 is 5.92 km, station 2 to station 3 is 6.19 km and station 3 to station 4 is 10.9 km. The sampling locations were not evenly demarcated, rather choice of sampling locations were based on accessibility to the river.

Field sampling: River bed sediments were collected from the surface along the mainstream for three months with a bottom grab sampler. A 6-inch Ekman grab was forced into the substratum and the contents trapped by the grab were immediately emptied separately into pre-cleaned polyethylene bags and labeled. At each station, three sediment samples were collected to maintain the accuracy of the findings. All the samples were stored separately in pre-cleaned polyethylene bags and stored in a dark-colour box containing ice blocks to prevent changes in chemical composition of the sediment and then transported to the laboratory for analysis.

Laboratory studies

Preparation of sediment samples for geochemical analysis: Samples obtained from the field were placed separately in metal plates and placed in a regulated oven at temperature of about 45°C for 24 h to remove moisture content. To disintegrate the coarse samples, the dried samples were respectively crushed in a jaw crusher. To further reduce the sample to fine power, the crushed samples ware respectively crushed with mortar and pestle, cleaning the mortar and pestle at intervals to avoid cross contamination. To arrive at carefully defined particle size, the crushed samples were respectively sieved with a laboratory sieve of mesh size of 90 µm. Each of the powdered samples was carefully put in drug envelope with sample number.

Digestion and sediment analysis: Lead (Pb), Cobalt (Co), Nickel (Ni), Chromium (Cr), Iron (Fe), Manganese (Mn), Mercury (Hg) and Zinc were determined by atomic spectrophotometer. For digestion, 2 g of dried samples was put into a PTFE vessel with 4 mL of HNO_3, 2 mL of HCl and 2 mL of hydrofluoric acid. After digestion and cooling below extractor hook, samples were filtered and diluted to 100 mL with water and analyzed.

Table 1. Composition of metals in sediments of Akpa Yafe River, Bakassi, Cross River State, Nigeria.

Parameters	Location 1 (Ikang)	Location 2 (Esuokon)	Location 3 (Ifiang Ayong)	Location 4 (Archibong)	Mean value±SD
Hg (mg/kg)	0.004±0.001	ND	ND	ND	0.001±0.001
Co (mg/kg)	0.005±0.001	0.003±0.006	0.004±0.006	0.001±0.006	0.003±0.005
Mn (mg/kg)	0.011±0.002	0.004±0.001	0.005±0.001	0.004±0.006	0.006±0.002
Cd (mg/kg)	0.002±0.001	0.002±0.001	0.001±0.006	0.002±0.001	0.002±0.002
Ni (mg/kg)	0.521±0.004	0.247±0.005	0.232±0.004	0.245±0.004	0.311±0.004
Fe (mg/kg)	0.414±0.006	0.117±0.003	0.125±0.002	0.125±0.004	0.195±0.003
Pb (mg/kg)	0.037±0.002	0.011±0.001	0.012±0.001	0.011±0.002	0.018±0.001
Zn (mg/kg)	0.009±0.002	0.004±0.001	0.006±0.002	0.005±0.002	0.006±0.002

ND = Not detected.

Statistical analysis: Data obtained were subjected to descriptive statistics. The values were computed and recorded as mean ± standard deviation and presented in tables and charts.

Results

The summary of the concentration values of metals in Akpa Yafe River sediments of the study area is presented in Table 1. Mercury (Hg) was detected only at station 1 with a mean value of 0.004 mg/kg. Cobalt (Co) was detected in all the stations with average concentration value of 0.003 mg/kg. The highest concentration of Co was recorded at station 1 (0.005 mg/kg) while, the lowest concentration was recorded at station 4 (0.001 mg/kg). Manganese (Mn) concentration value (0.11 mg/kg) was highest at station 1 and lowest at stations 2 and 4 with mean value of 0.004 respectively. Cadmium (Cd) concentration values were highest at stations 1, 2 and 4 with concentration value of 0.002 mg/kg in the three stations. The concentration of Ni was highest at station 1 (0.521 mg/kg) while, the lowest concentration was recorded at station 3 (0.232 mg/kg). Iron (Fe) highest concentration value (0.414 mg/kg) was recorded at station 1 and the lowest value (0.117 mg/kg) was recorded at station 2. Station 1 had the highest concentration value (0.037 mg/kg) of Pb while, stations 2 and 4 recorded the lowest concentration values (0.011 mg/kg) respectively. Highest concentration value of Zn was recorded at station 1 (0.009 mg/kg) while, the lowest concentration was recorded at station 2 (0.004 mg/kg). Station 1 recorded the highest concentration values of all the metals analyzed.

Variations in months of the concentration of metals in the four stations of Akpa Yafe River during the sampling period (Aug-Oct 2012) are presented in Figs. 2-9. The highest concentration value (0.005 mg/kg) of Hg was recorded in Oct at station 1. Concentration value of 0.001 mg/kg in Aug and Oct were recorded at stations 2 and 3 respectively while, other months at stations 2, 3 and 4 recorded 0.000 mg/kg respectively (Fig. 2). Cobalt (Co) concentration values were highest in Aug (0.006 mg/kg) at station 1 and lowest in Aug (0.001 mg/kg) and Sep (0.001 mg/kg) at station 4 (Fig. 3).

Fig. 2. Variations in Mercury (Hg) levels in the four sampling stations of Akpa Yafe River.

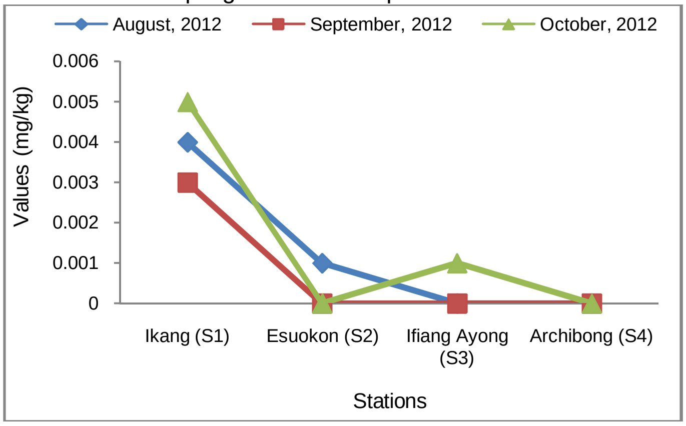
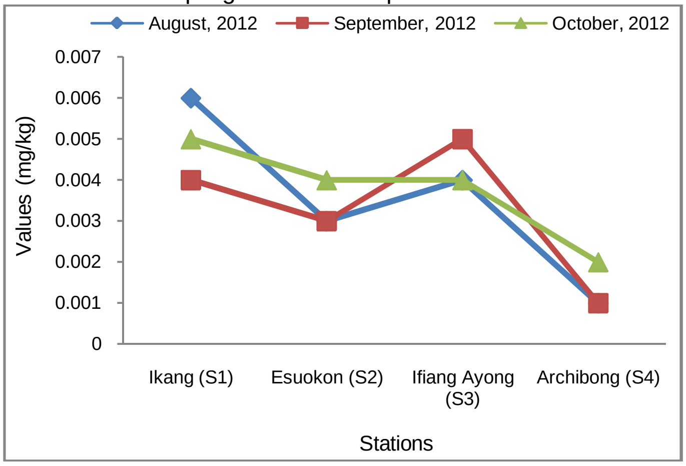


Fig. 3. Variations in Cobalt (Co) levels in the four sampling stations of Akpa Yafe River.



The highest concentration value of Mn was recorded in Sep (0.012 mg/kg) and Oct (0.012 mg/kg) at station 1 while, the lowest concentration value was recorded in Sep (0.003 mg/kg) at station 2 (Fig. 4). Variation in Cd concentration level is shown in Fig. 5. The highest concentration value was recorded in Oct at stations 1, 2 and 4, all measuring 0.003 mg/kg. The lowest concentration values were recorded in Sep (0.001 mg/kg) at station 1, Aug (0.001 mg/kg) at station 2, Aug and Sep (0.001 mg/kg) respectively at station 3 and Sep (0.001 mg/kg) at station 4.

Fig. 4. Variations in Manganese (Mn) levels in the four sampling stations of Akpa Yafe River.

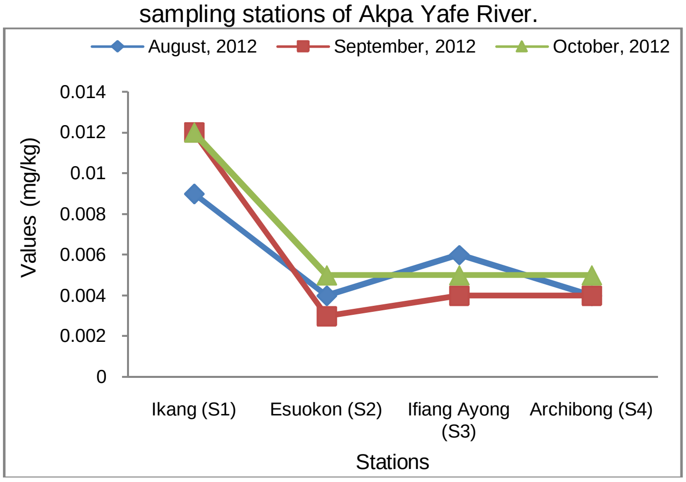


Fig. 7. Variations in Iron (Fe) levels in the four sampling stations of Akpa Yafe River.

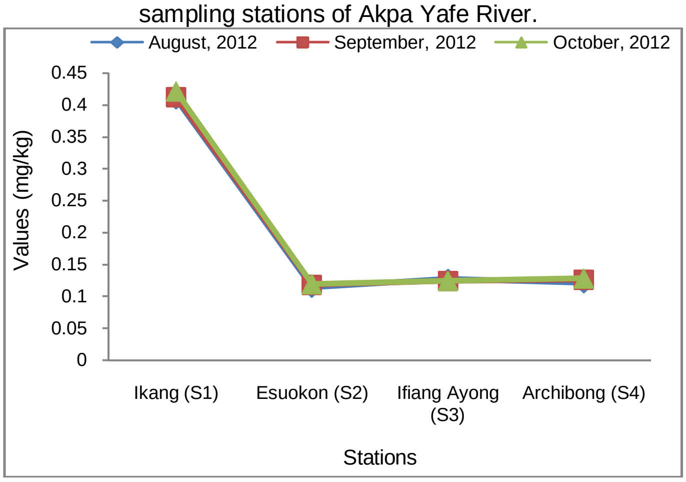


Fig. 5. Variations in Cadmium (Cd) levels in the four sampling stations of Akpa Yafe River.

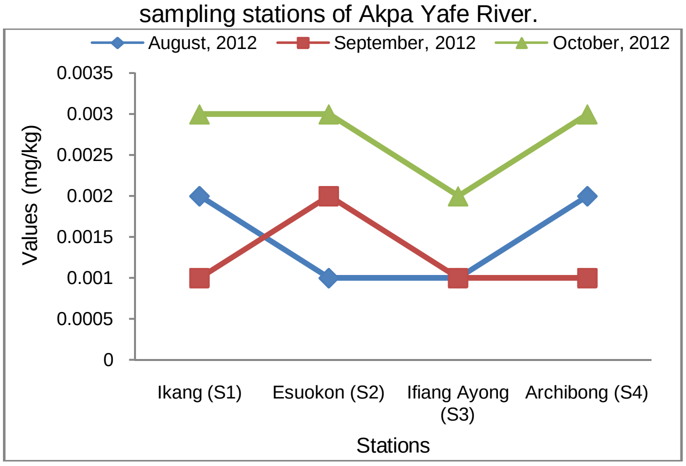


Fig. 8. Variations in Lead (Pb) levels in the four sampling stations of Akpa Yafe River.

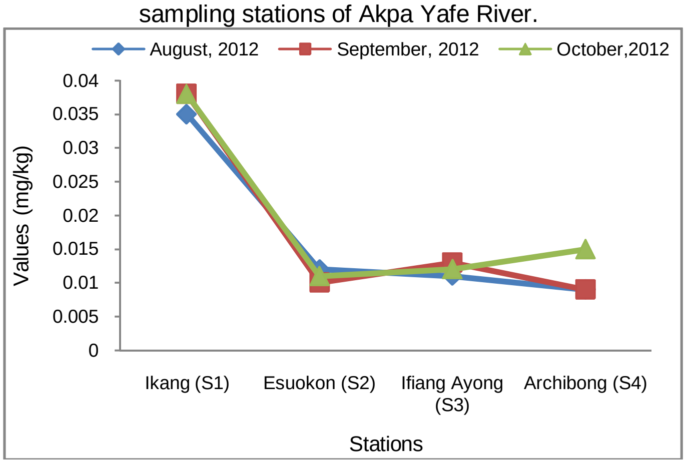


Fig. 6. Variations in Nickel (Ni) levels in the four sampling stations of Akpa Yafe River.

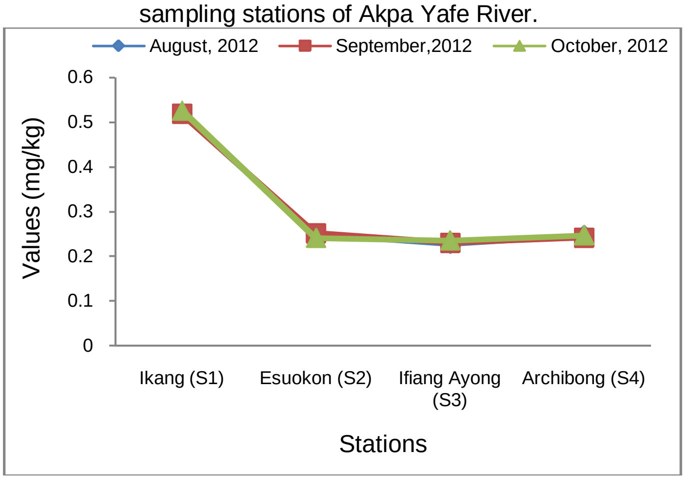


Fig. 9. Variations in Zinc (Zn) levels in the four sampling stations of Akpa Yafe River.

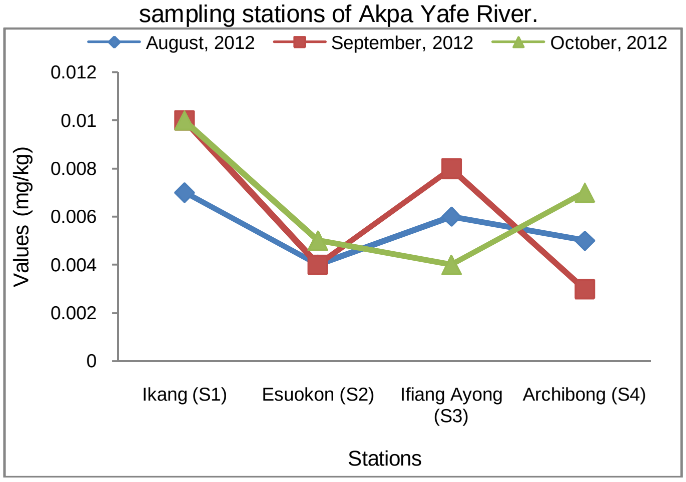


Figure 6 shows the variation in concentration levels of Ni in the sampling stations. Ni concentration values were highest in Oct (0.526 mg/kg) at station 1 and lowest in Aug (0.228 mg/kg) at station 3, although the variations were very narrow. Iron (Fe) concentration level was highest in Oct (0.421 mg/kg) at station 1 and lowest in Aug (0.114 mg/kg) at station 2 (Fig. 7).

Lead (Pb) concentration values were highest in Sep and Oct with concentration values of 0.038 mg/kg respectively at station 1 while, the lowest concentration values were recorded in Aug and Sep with concentration values of 0.009 mg/kg respectively at station 4 (Fig. 8). Variation in Zn level is presented in Fig. 9.

The highest concentration values were recorded in Sep and Oct with concentration values of 0.01 mg/kg respectively at station 1 while, the lowest concentration value (0.003 mg/kg) was recorded in Sep at station 4.

Discussion

The high concentration of Ni compared to other meals in this study could be attributed to domestic discharge on surface water. This element has also occurred as one of the prominent heavy metals in other studies of sediments in the coastal areas (Nwadiaro and Odigi 1991; Okuo and Iyasele 2004). Contamination of heavy metals in the sediments were in the following order: N_i>F_e>P_b>M_n>Zn>C_o>Hg. Generally, concentrations of all the metals at the study sites were observed to be moderately normal, this is indicative of moderate level of anthropogenic metals input into the river. The levels of metals at each site demonstrate the extent to which each location receives anthropogenic metallic wastes. High level of metals in any aquatic ecosystem is of environmental significance and it is indicative of a continual imputing of anthropogenic metal burden into the environment. Majority of such metals may persist and thus become toxic not only to aquatic lives but also humans who are at the top of the food chain. In addition, natural (run off from non point sources) and human related activities are major contributing factors to higher metal loading. Apart from Ni and Fe which recorded average concentrations of 0.311 and 0.195 mg/kg respectively (Table 1), all other metals were recorded at concentrations below WHO average levels for rivers and soils (Pais and Jones, 1997).

Zinc is an essential nutrient that is needed by the body for several reasons. It is considered as one of the most abundant trace metals in the body. Based on recommended daily dietary allowance of 5 mg/d in infant and 10/15 mg/d in children/adult (NAS, 2001), zinc was detected below health guidelines across the entire study areas. This suggests that eating fish and benthic organisms from the various locations of the river on a daily basis would not result in harmful health effect due to zinc if the level does not increase above the present level. Accumulation of Pb in sediment is of serious environmental concern. Age among humans remains a major factor in determining the extent of Pb absorption. More lead has been reported to enter bloodstream of children than adults through consumption of Pb-contaminated fish (ATSDR, 1999). This is probably due to higher rate of detoxification (≈99%) of the metal in adult and elimination through the faeces and urine compared to 65% being detoxified in children. The range of mean concentration of Pb obtained in the study (0.00-0.004 mg/kg) is not of serious concern. This is based on the fact that the tolerable daily intake of Pb is 25 µg/kg body weight which is above the range of Pb concentration in the study. On the average, the concentration of lead (0.001 mg/kg), cobalt (0.003 mg/kg), manganese (0.006 mg/kg) and other metals detected vary from one location to another. This could be attributed to geological distribution of minerals that vary from one location to the other. Similar variations were reported in sediment of major dams in Ekiti State (Adefemi *et al.,* 2007). The metals reported from sediments in Okirika River (Okuo and Iyasele, 2004) were different and higher than those in Akpa Yafe River. The different human activities along the river banks may have accounted for the differences. The study of sediments in Ikpoba River in Benin City showed that Cd, Co, Cu, Fe, Ni, Mn and Zn were present in the sediments (Oguzie, 2000), an indication that those metals are widely distributed in the region. Study on sediment samples in the Niger Delta region of Nigeria also showed similar metal concentrations like the one found in Akpa Yafe River (Odokuma and Ijeoma. 2003; Okuo and Iyasele, 2004). However, the levels obtained in Akpa Yafe River are considerably lower than concentration obtained in some studies within and outside Nigeria (DeCarlo *et al.,* 2005; Ololode *et al.,* 2007; Nuria *et al.,* 2008).

Conclusion

All living organisms are in continuous interactions with their environments. Any negative impact on the environment can directly or indirectly affect the organisms that depend on such environments for their survival. Metals entry into the environment can cause deleterious or hazardous impact on the organisms exposed. Such impacts as bioaccumulation and toxicity can disrupt ecological process within food chain and food web. Therefore, efforts should be geared towards avoiding the aquatic systems from exposure to contaminants or pollutants. Majority of our rivers, lakes and oceans sediments have been contaminated by pollutants. Some of these pollutants are directly discharged by industrial plants and municipal sewage treatment plants, others come from polluted runoff in urban and agricultural areas and some are as a result of historical contamination (Pandey, 2003). Contaminated sediments can threaten creatures in the benthic environment, exposing worm crustaceans and insects to hazardous concentration of toxic sediment, kill benthic organism, reducing the food available to large animal such as fish. Some contaminants in the sediment are taken up by benthic organisms in a process called bioaccumulation. When large 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 shell fish, water fowl, fresh water ducks and marine mammals may accumulate hazardous concentration of toxic chemicals found in the sediment. Sediment pollution has been of much concern during the last few decades due to the adverse effect of some metals on living organism in food chains which have man as the ultimate. Discharges from non-ferrous metal production can also pollute sediment, though these elements are consistently present in trace amounts in the environment; they are potentially toxic and could affect the biota at water-soluble concentration of less than 1 ppm (Freedman, 1989). Also, the doses received by a target organism is not only a function of the concentration, but also a function of the period of exposure (Freedman, 1989), cadmium has both long and short term effect on specific tissues/organs of the body. Lead causes damage to a variety of organs with significant effects it affects the kidneys, bones, gastrointestinal tract and the nervous system and causes blindness (Timbrell, 1991). Contaminated sediments do not always remain at the bottom of a water body. Anything that stirs up the water, such as dredging, can re-suspend sediments. Re-suspension may be that all of the animal in the water and not just the bottom-dwelling organism will be directly exposed to a toxic contaminant.

The results of the assessment of chemical composition of sediment in Akpa Yafe River could be used as a baseline and reference point for assessing further changes caused by nature or man in this river, since there has not been published information on this important river. Also, the villagers should be enlightened through public awareness programmes to teach them the ecological consequences of polluted water on aquatic components (biotic and abiotic) and also the health implications on humans. Maintaining an adequate in-stream flow is critical to protecting water quality and preserving aquatic habitat. Use of best management practices can also help villages, utilities and landowners avoid harm to aquatic systems. This includes cautious use of pesticides and herbicides. Farmers should be taught how to apply the right amount of the right fertilizers at the right moment, and know that it would go directly into their crops and not into the river. Dumping of refuse into the aquatic systems should be avoided. Sewage and effluents should be treated to detoxify them because they will end up in our aquatic ecosystems.

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