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Spatial Distribution of Some Heavy Metals in Sediments from the River Hadejia Catchment, Nigeria

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Abstract

Heavy metals concentration levels was determined using Instrumental Nitrogen Activation Analysis (INAA) is possible using Nigeria Research Reactor-1 (NIRR) which is a Miniature Neutron Source Reactor (MNSR). It is specifically used for the Neutron Activation Analysis (NAA) technique. The selection of sediment sample is because, overtime, the chemical elements precipitate on the sediment bed; therefore the sediment sample will indicate the true nature of the chemical elements present in the river system. River Hadejia is a perennial river, though the dry season flow is from the upstream regulated flow from the Tiga and Bagauda dams. The sediment samples were collected using stratified random sampling technique based on change in land use activity. Samples were collected during dry and wet seasons and analyzed in the laboratory. The results obtained show the presence of chemical contaminants Chromium (Cr), Zinc (Zn), and Europium (Eu) in concentrations above the permissible limits in the Hadejia river system. For example, Chromium (Cr) has mean concentration of 432.86 mg/l *as against the permissible limit for both WHO, (2011) and NSDWQ, (2007) of 0.05mg/l.Anthropogenic and natural geology of the area are the key determinants of the presence of these chemical elements in the area. It is recommended among others that there is need for routing the actual sources of these contaminants in our river catchment areas.*

Keywords: River Hadejia; Chemical contaminants; Sediment; Instrumental Neutron Activation Analysis (INAA); Evaluation.

1.0 Background of the Study

Water is important for maintaining a vibrant economy. Most industries require water for their production processes. Many industries also use water in processing raw materials such as in the food and beverages, pharmaceutical, tannery and textile industries. They also use water for their waste transportation and disposal. Water is also used for agricultural purposes such as fish farming, irrigation, livestock rearing and so on which provide employment opportunities and revenue.

The over exploitation of groundwater as well as pollution of ground and surface water by human activities like dumping of toxic substances and solid wastes into the water body; the washing of agrochemicals and fertilizers applied to farms by erosion and runoff into streams and rivers causes a serious concern for water resources management. Also, with the increase in world population, which has led to increase in developmental activities such as increase in industrial production, increase in agricultural activities and urbanization, there has been an increase in waste generation from industrial, agricultural, and domestic sources. All these wastes end up directly or indirectly into rivers and streams which serve as sources of water supply for communities and cities. The continual introduction of harmful, unwanted, and unhealthy substances into water bodies deteriorates their quality. When consumed or used, such water can have adverse effects on the community or individual user. This justifies the need for continuous water quality evaluation of our water bodies such as streams, rivers and lakes in order to determine the true nature and quality of the water body and to identify the source region of the pollutants.

The quality of water depends on the management of anthropogenic discharges as well as the normal physicochemical characteristics of the catchment areas (Efe *et al.*, 2005). Both natural conditions and human activities affect water quality of available water resources. Through his various socio-economic and industrial activities, man has caused severe water pollution of variable environmental problems; such as diseases, sudden deaths, and disabilities. Water related diseases such as dysentery, diarrhea, bilharziasis, typhoid fever, cholera, guinea worm and so on are very common among communities that live close to polluted river sources which flow through large urban areas. In Kano, for example, the Challawa River which drains the densely populated residential area (southern part of metropolitan Kano) and industrial areas (Sharada and Challawa) usually appears to be highly polluted (Fieldwork, 2013).

1.1 Impacts of Human Activities on Water Quality

The presence of some toxic metals in our rivers is posing a serious challenge to our society. Though some of such metals occur naturally (as a result of geological processes like weathering, leaching), others occur due to some human activities (like burning fossil fuels, mining, industrial, and agricultural discharges)' Bichi, et al (2009). 'Once present in an environment, metals are not usually removed rapidly, nor are they readily detoxified by metabolic activity; as a result, they accumulate (Duffus,1980;Lentech, 2011).

There are many ways through which surface water can be polluted, but the degree of pollution will depend on the socioeconomic status, population density, and hygienic habits of the population. Three major human activities were identified as the major ways through which man tamper with the quality of water resources especially in urban areas. They include:-

- Agricultural Activities
- Industrial Activities
- Residential Activities

Those rivers which flow through urban centres are being heavily polluted by domestic, agricultural, and industrial pollutants in gaseous, liquid, and solid forms (Ajayi and Adeleye 1977;Osibanjo, 1979;Ekundeye, 1977 as cited in Nwosu, 1983). In the world today, the rapid increase in population, urbanization and industrialization has brought about increase in demand of water and equitably a drastic rise in water pollution. Population pressures will increase demand for food, this implies that more fertilizers, herbicides, and pesticides had to be applied on to the soil and crops, out of which some percentage of such chemical constituents leached or drain directly into surface waters and makes the water highly polluted; therefore, this implies that the more the population, the more the pollution' (Mogekwu, 1996 as cited in Ajura, 1996).

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1.2 Statement of the Research Problem

The Hadejia River catchment comprises of Rivers Hadejia, Kano, and Challawa. These also have a number of small rivers as their tributaries including Watari, Tatsawarki, Salanta, Shimar, Dukku, Dori, Kamanda and Yarkato. This watershed is the main source of water supply for the over five million people in the metropolitan Kano and other neighbouring towns and villages. It also provides water for irrigation in the Kano River Irrigation Project (KRIP) and the Hadejia Valley Irrigation Project (HVIP). Fishing and recreation are also important activities in this area.

The various socio-economic activities in Kano and its environs lead to increasing deterioration of the water quality in the Hadejia river catchment. A number of industrial, residential and commercial establishments are developing within the catchment area of the river and are continually discharging wastes into these water courses. The increasing level of water pollution by chemical contaminants from various human activities is at alarming rate. Rain fed cultivation, irrigation agriculture and market gardening going on along the banks of these rivers also contribute various kinds of wastes into the rivers.

1.3 Objective of the Study

The study aimed to assess, identify and determine the types and levels of concentration of some chemical contaminants in the river Hadejia sediments.

2.0 THE STUDY AREA

The area covered by this study is the polygon covered by longitudes and latitudes E $8^0$07'50.0'' N $11^0$32'08.4'' and the E$10^0$01'50.9'' N $12^0$26'24.8'' (which extend up to Jigawa State refer to Figure 1 and Table 1). Urban Kano or Kano metropolis is located between latitudes $11^0$50'N to $12^0$2'N and longitudes $8^0$22'E to $8^0$40'E. The study covers the long profile of the Hadejia river, which covers the southwestern tip of Kano (area of Falgore game reserve near the source of Kano River system), the western tip near the source of the Challawa system, and the extreme northern tip of Jigawa state. The Hadejia River catchment covers an area of about 32,900 km^2 (Sobowale *et al*, 2010).

The Hadejia River system got its sources from the foothills of the Jos Plateau and flows down to Tamburawa where it joined Challawa in southern part of Kano State. It runs vertically to the north, until it reached the upland of Kano it joined Challawa and flow eastern direction. The Falgore game reserve which protected the sediment yields down slope, serve as a filter to the Tiga dam which was built across the river. However, human intervention on the forest resources and residential areas is making the watershed vulnerable. The Kano river basin in the south of the city comprises of the Kano and Challawa Rivers. These also have a number of small rivers as their tributaries including rivers Watari, Tatsawarki, Shimar, Dori, Dukku, Kamanda, Salantan and Yarkato. This basin is the main source of water supply for metropolitan Kano and other neighbouring towns and villages as well as water for irrigation in the Kano river project and the Watari dam project. Three of the most important dam/reservoirs in the region (Tiga, Challawa gorge, and Watari) are located in this basin. River Kano and its tributaries are the receiving waters for the southern part of the urban Kano. A minimum flow is maintained in the river throughout the year by the Tiga and Challawa gorge dams. Tube wells drilled in the bed of this river provides water for the 90 million m^3/day treatment plant at Tamburawa. The same river also provides water for the new 150 million litre/day water treatment plant at Tamburawa since 2007. The Wudil and Hadejia regional water treatment facilities are also located in this catchment. The river through its tributary the river Yarkato, receives the effluents discharged from the Sharada industrial estate and the neighbouringDorayi residential area, discharging just upstream of the Challawa water intake. River Tatsawarki and its tributary river Salantan is the main drain of southern part of Kano with no natural flow in the dry season. The river receives the entire raw wastewater from Sharada phase 1 industrial area as well as wastewater from the residential areas of Tarauni, GandunAlbasa, Gyadi-Gyadi, Naibawa and Kumbotso.

Table 1. Geography of the Sampling Points.

Sampling Points	Type of Land use/Discharge	Relative Location	Longitude	Latitude	Elevation (m)
KNRS01	Residential	Gyadi-Gyadi behind AKTH	E 8^{O}31’29.0’’	N1 1^{O}57’48.7’’	479
KNRS02		Kumbotso near Works	E 8^{O}30’15.0’’	N1 1^{O}53’01.3’’	454
KNIN01	Industrial	Sharada near Freedom Radio	E 8^{O}30’39.9’’	N1 1^{O}57’34.0’’	466
KNIN02		Challawa behind Cocacola	E 8^{O}28’19.7’’	N1 1^{O}53’08.9’’	449
KNAI01	Agricultural (Irrigated)	KRP near DanHassan, Kura	E 8^{O}31’42.3’’	N1 1^{O}46’24.8’’	430
KNAI01		Hadejia near bridge1	E10^{O}01’50.9’’	N12^{O}26’24.8’’	363
KNAC01	Agricultural (Cultivated)	Dukku near Yaryasa	E 8^{O}18’08.6’’	N1 1^{O}20’47.9’’	531
KNAC02		Yakasawa near Ringim	E 9^{O}10’07.4’’	N1 2^{O}07’35.4’’	396
KNAF01	Agricultural (Forested)	Dansoshiya Forest near Dangora	E 8^{O}07’50.0’’	N1 1^{O}32’08.4’’	559
KNAF02		Falgore Game Reserve near Doguwa	E 8^{O}36’55.8’’	N1 1^{O}01’03.9’’	590
KNRW	Raw Water (before treatment)	Raw water intake at Tamburawa (WTP)	E 8^{O}30’44.7’’	N1 1^{O}50’32.6’’	435

Source: Fieldwork (2013).

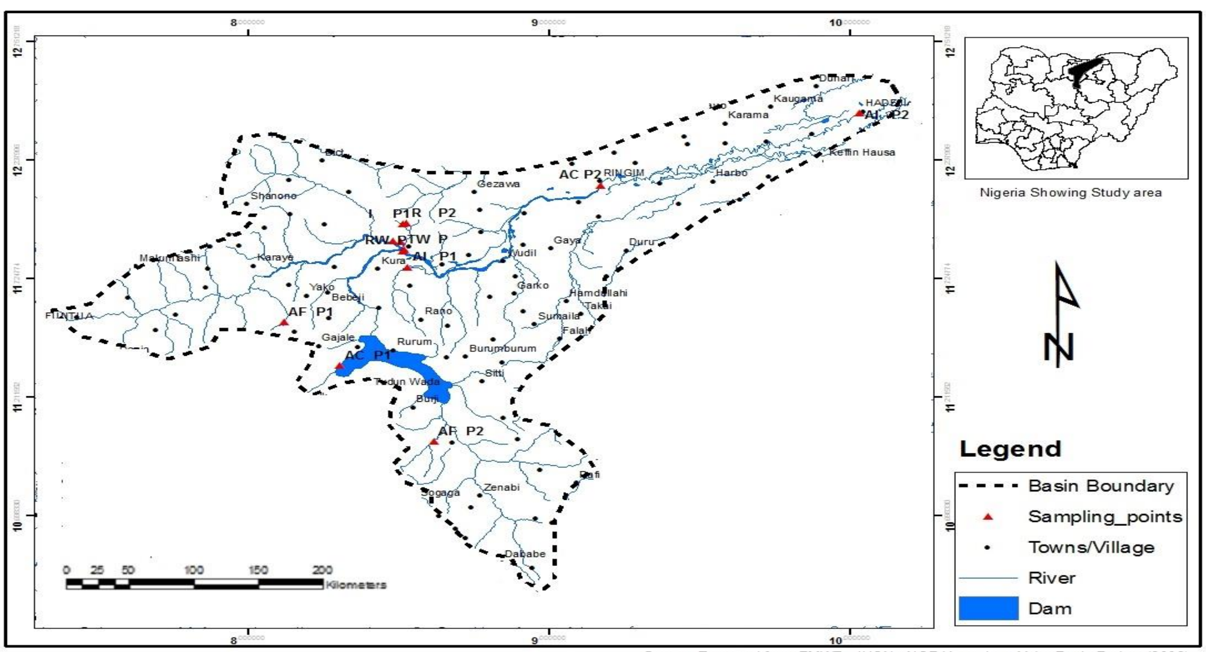

Figure 1. Geographical location of the area. Source: Yobe Basin Project (2006).

3.0 MATERIALS AND METHODS

A preliminary study was conducted in order to get acquainted with the study area, with a view of selecting the sampling points. Various land-use activities were identified before deciding on where to obtain the samples. ST 2276 GPS was used to determine the absolute location as well as the elevation of each point above sea level.Samples were obtained using stratified systematic sampling technique. The sampling period was divided in to dry and wet season.

3.1 Water Quality Criteria

One very important aspect of water quality considered for laboratory investigation is chemical contaminants. This is because trace elements (metals) are potentially toxic and disastrous when present in water even in minute concentration. They are not easily detected and removed by the traditional water treatment facilities. Instrumental Neutron Activation Analysis (INAA) technique was used for the analysis of the sediment samples for the following trace metals. They vary in toxicity and harmfulness; they include Cadmium (Cd), Copper (Cu) and Nickel (Ni).

3.2 Data Collection Process

Sediment samples were collected during peak of dry and wet seasons. This is because river water is more dynamic always moving thereby changing frequently; but for the sediments, over time, the chemical elements precipitate on the sediment bed and accumulate thereby acting as a sink for pollutants. It was opined by Taiwo, *et al* (2012) that 'accumulated heavy metals or organic pollutants in sediment could be released back into the water with deleterious effects on human health'. The selection of sediment sample is because, overtime, the chemical elements precipitate on the sediment bed; therefore the sediment sample will indicate the true nature of the chemical elements present in the river system. Also, concentration of heavy metals in water depends on its hydrogen exponent; their solubility is greatest in acid water than alkaline water. When after some distance from the source of pollution hydrogen exponent increases, heavy metals tend to precipitate. But then, they accumulate and magnify on the sediment bed, alluvium or in cultivated soil, and when hydrogen exponent of water changes for more acid, they can be remobilized and enter again into the water (Garba, 2014). The accumulation of heavy metals in the bottom sediments of river bodies and their remobilization are two of the most important mechanisms in the regulation of pollutant concentrations (Linnik and Zubenko, 2000). In the past however, water quality studies focused mainly on the detection of contaminants in the water column and ignored sediments, whereas it represents one of the large and ultimate sinks or reservoirs for metals discharged into environment (Hollert*et al*., 2003; Audry*et al*., 2004; Beg and Ali, 2008; Abbas *et al.*, 2009).

The sediment samples were collected at each sampling point using sediment core sampler. The samples were acidified with 2 ml of Nitric acid to suppress growth of microorganisms during transportation/storage (MARLAP, 2004).

The Instrumental Neutron Activation Analysis (INAA) is a sensitive multi-element analytical technique used for major, minor, trace and rare elements. INAA was discovered in 1936 by Hevesy and Levi, who found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons (http://archeometry.missouri.edu/naa-overview.html). This observation led to the use of induced radioactivity for the identification of elements. INAA is significantly different from other spectroscopic analytical techniques in that it is based not on electronic transitions but on nuclear transitions. To carry out an INAA analysis, the specimen is placed into a suitable irradiation facility and bombarded with neutrons, this creates artificial radioisotopes of the elements present. Following irradiation, the artificial radioisotopes decay via the emission of particles, or more importantly, gamma rays, which are characteristic of the element from which they were emitted (Oladipo*et al*, 1994; Omenesa, 2011).

The INAA is possible using Nigeria Research Reactor-1 (NIRR) which is a Miniature Neutron Source Reactor (MNSR). It is specifically used for the Neutron Activation Analysis (NAA) technique. The NIRR-1 is a low power nuclear reactor using highly enriched uranium as fuel, light water as moderator and beryllium as reflector. The associated facility for radioactivity measurements is aHPGe detector system. It consists of a horizontal dip-stick Highly-Purity Germanium (HPGe) detector with a reflective efficiency of 2% at 1332.5 kev gamma ray line; the MAETRO emulation software compatible ADCAM multi-Channel Analyzer (mCA) card, associated electronic modules all made by EG & G ORTC and a personal computer (Butu, 2011). Activation analysis is a nuclear method of determining the concentrations of elements in a wide variety of materials. The sample is first made radioactive by bombardment with suitable nuclear particles, then the radioactive isotopes created are identified and the element concentrations are determined by the gamma-rays they emit. The most common particle employed is the neutron thus, the method is known as Neutron Activation Analysis (NAA). It is capable of detecting many elements at extremely low concentrations.

The main advantage of NAA over analytical spectroscopic methods is that since neutrons "activate" the nucleus of an atom, not the electron shell, this method "sees" the total elemental content, regardless of oxidation state, chemical form or physical location. Neutrons have no charge and will pass through most materials without difficulty. Therefore the centre of the sample becomes just as radioactive as the surface. This technique remains at the forefront of techniques for the quantitative multi-elemental analysis of major, minor, trace and rare elements.

4. 0 RESULTS AND DISCUSSION

Chromium (Cr)

Chromium is a widely distributed metal. 'It is contained in small amounts of most rocks and soils' (Musa, 1990). It is an essential micronutrient in trace quantities for fat and carbohydrate metabolism in living organisms. 'In industry, it is used in making steel alloys, in chromium plating and in leather tanning (Duffs, 1980).

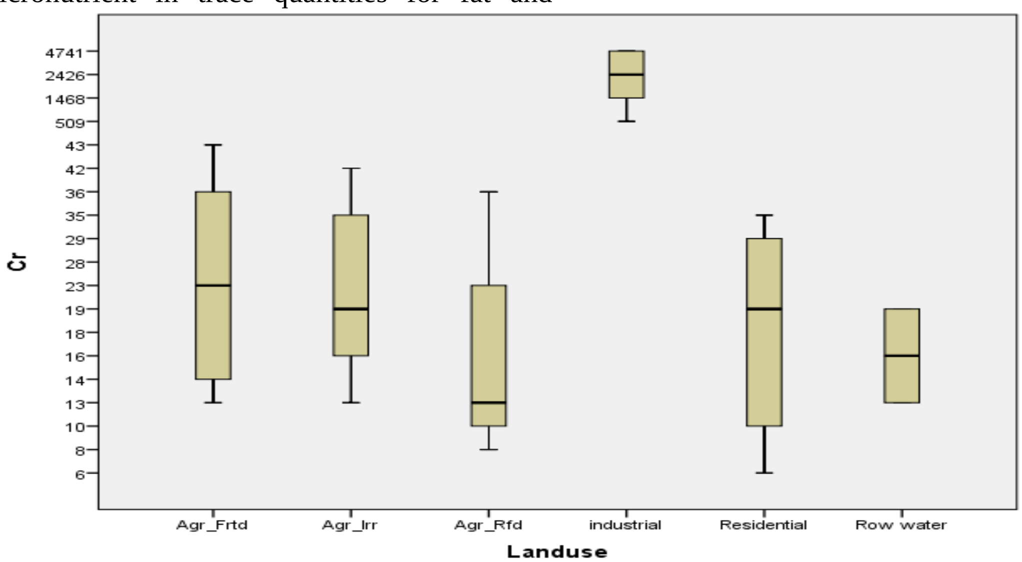

Figure 2. Spatial Variations in Concentration of Cr along Hadejia River.

The mean concentration of Cr in the Hadejia River is 432.86 mg/l with STDV 11.83 mg/l (see Figure 2). The highest mean value of 2286.00 mg/l and was recorded at the Industrial area; while the lowest mean value of 16.00 mg/l was recorded at the raw water point. The outstanding concentration of Cr in the industrial area could be due to its discharge in the tannery sludge from the tannery industries in the study area. In the Challawa industrial area, there are many functional tannery industries like Globus Tannery, Multitan limited, Ayafa Concepts and Tannery, Gods' Little Tannery, Mario & Co, White Gold, Luquat Tannery and so on.

The presence of Cr in other locations in the Hadejia river catchment could be attributable to its natural occurrence in the geology of the area and possible dissolution of Cr bearing minerals beneath the river bed.

Zinc (Zn)

Zinc is an essential micronutrient which makes up only about 0.004% of the earth's crust. It's most important use is as a protective coating on other metals, particularly in galvanizing iron and steel. Though it is generally considered as a less hazardous element, its toxicity may be enhanced by the presence as impurity of some toxic metals like arsenic, lead, cadmium and antimony. Due to its toxic effects at certain concentrations, it is not recommended to store food in zinc or galvanized containers but acceptable for drinking water. This is because acidic foods can dissolve enough zinc to cause poisoning. 'a factor which serves to minimize the risk of zinc poisoning is that it appears to be lost along food chains, unlike methyl-mercury or cadmium, for example which accumulate' (Duffus, 1980).

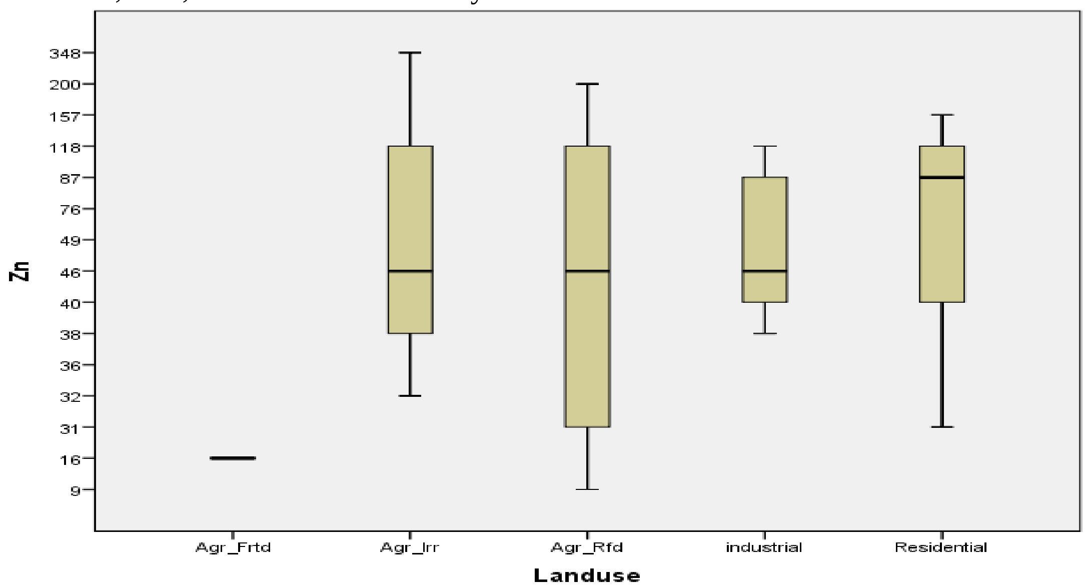

Figure 3. Spatial Variations in Concentration of Zn along Hadejia River.

The mean concentration of Zn in the Hadejia River is 81.19 mg/l with STDV 89.07 mg/l (see Figure 3). The highest mean value of 142.00 mg/l and was recorded at the Agricultural Irrigated area; while the lowest mean value of 16.00 mg/l was recorded at the Agricultural Forested area. Its presence in the irrigated and rainfed areas could be linked to the use of some additives to the soil by farmers to improve the Zn nutrient content. The spatial presence of Zn in the Hadejia river catchment could be attributable to its natural occurrence in the geology of the area.

Europium (Eu)

It is one of the less abundant rare earth elements and is never found in nature as free element, but there are many elemental ores containing Eu (Lenntech, 2009).

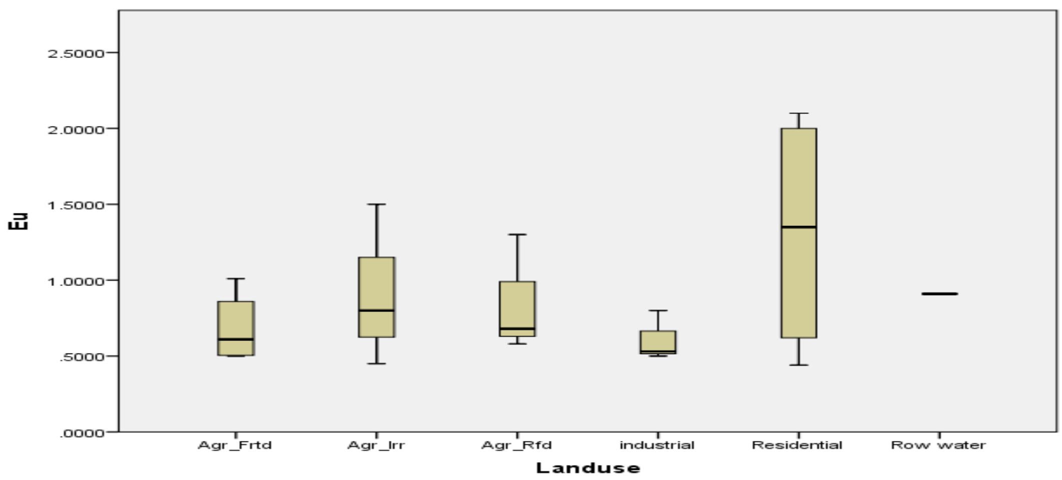

Figure 4. Spatial Variations in Concentration of Eu along Hadejia River.

The mean concentration of Eu in the Hadejia River is 0.89 mg/l with STDV 0.50 mg/l (see Figure 4). The highest mean value of 1.31 mg/l and was recorded at the Residential area; while the lowest mean value of 0.61 mg/l was recorded at the Industrial area. The high Eu concentration in the Residential area could be from wash offs from domestic effluents. The spatial presence of Eu in the Hadejia river catchment could be attributable to its natural occurrence in some elements containing it in the area.

5.0 CONCLUSION

It may be concluded from the findings that there is clear distinction in the impact of landuse activities on the chemical water quality in the river Hadejia catchment with industrial activities having highest contribution. The results obtained show the presence of some toxic metals in concentrations (more particularly Cadmium) above the permissible limits in the watershed. This call for a very rapid intervention in order to save the lives of millions of people living in this river catchment area.

5.1 Recommendations

Many organizations and governments especially in developed nations where severe chemical pollution from several land use activities (especially industrial) have caused deaths, deformations and other health hazards have made several recommendations to safeguard public health. These range from planning, policy formulation and enforcement, to management of water resources watersheds. The above is a general recommendation. But for the peculiar nature of pollutants generation and nonchalant attitude of residents of some parts of Kano region to the sanitary ethics, the following suggestions are recommended:

- There should be proper monitoring of our industries to ascertain the degree of compliance to the in-house treatment and permissible effluent discharges limit; defaulters should be sanctioned appropriately.
- The use of mass media for propagating environmental education with emphasis on impacts of indiscriminate waste discharge on water quality, public health and the environment.

There should be continuous periodic water quality assessment of the river because of the dynamic nature of human activities taking place in the watershed, for efficient planning and management of our surface water resources.

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