Concentration of Metal Pollutants in River Kubanni, Zaria, Nigeria.

Ali Williams Butu Department of Geography Ahmadu Bello University Zaria, Nigeria. E-mail: alibutu@yahoo.com

Abstract

The study focused on concentration of metal pollutants in River Kubanni Zaria, Nigeria. The main sources of data for the study were sediments from four different sampling locations along the long profile of the river. The samples were prepared in the laboratory according to standard method and Instrumental Neutron Activation Analysis (INAA) was adopted in the analysis of the data using Nigeria Research Reactor – 1 (NIRR -1). 29 metal pollutants; Mg, Al, Ca,Ti, V, Mn, Dy,Na, K,As, Br, La, Sm, Yb, U, Sc, Cr, Zn, Fe, Co, Rb, Cs, Ba, Eu, Lu, Hf, Ta, Sb and Th were indentified in the river at various levels of concentration. The result of the analysis showed that most of the metal contaminants in the river are routed to anthropogenic activities from the four different sections of the river, while few are routed to geologic formation in the catchment area. The presence of most of these metal pollutants in water may have severe health implication on the consumers because most metals are known to be carcinogenic to humans; therefore the study recommended that anthropogenic practices that produce these chemical elements in the catchment area be controlled.

Keywords: Anthropogenic activities, chemical elements, carcinogenic, geologic formation, Kubanni River, level of concentration, metals, pollutants.

1. Introduction

Metals are chemical elements that are solid at ordinary temperatures, opaque, except in extremely thin films good electrical and thermal conductors, illustrious when polished and have a crystalline structure in the solid state (Gaus, 2009). The common metallic elements are aluminum, tarium, beryllium, bismut, calcium, cerium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, manganese, mangnesium, mercury, molybdenum, nickel, osmium, palladium, platinium, potassium, radium, rubidium, silver, sodium, tantalum, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, and zinc. Metallic elements can combine with one another and with other elements either as compounds or solutions or as intimate mixtures. Metals have positive valences in most of their compounds, which means that they tend to donate electrons to atoms which they bond, they form basic oxides. Metals can form salts like chlorides, carbonates and sulphides by serving as reducing agents or electron donors. (Gaus, 2009). Naturally occurring metals such as thallium, copper, cobalt, vanadium, cadium, nickel, uranium, chromium, zinc, mecury, lead and iron are deposited in aquatic environment either in soluble or insoluble form along the river course.

Chemical elements are easily introduced into aquatic system as a result of chemical weathering of soil and rocks from volcanic eruptions and from a variety of human activities involving processing or using of metals and substances that contained metals. There are two different types of sources of these metal pollutants in our water bodies. Point source is a localized pollution where pollutants come from single identifiable sources. The second type of pollution sources are non-point sources (diffuse pollution), where pollutants come from dispersed sources and often difficult to identify sources (Lentech, 2006). Gamboa-Rodriguez *et al.*, (2012) observed that the presence of Pb and Zn in Tabasco Lagoon, Mexico was as a result of pluvial discharges from the city around the lagoon that washed rusted metal roofs and carry domestic discharges, paints and roof of insulation debris from building as well as oil and combustion particles from automobile combustion, this is a good example of diffuse pollution. The greater challenges facing the water supply profession today are the control and removal of poisonous metal contaminants. Water pollution occurs in various forms and is caused by different factors.

The major causes of water pollution in most countries of the tropics can be linked to human activities such as sewage and refuse disposal, industrial effluents, agricultural activities, mining and quarrying activities. The most common source of water pollution in developing nations is domestic sewage and refuse. Iguisi *et al.*, (2012) is of the opinion, that several chemical elements have their origin in the composing high refuse dumps that dot the landscape of the built up section of the catchment area of Kubanni (ABU) dam. Several other studies have also shown that a considerable number of chemical elements are leached from refuse dumps during raining season into ground water

and streams (Olofin, 1991). Mechanic workshops where used engine oil and petrol are continually discarded are also available sources of lead contaminant. Industrialization is another major source of chemical pollution; industrial effluents are discharged into water sources without treatment (Farouk, 1998). The discharge of domestic sewage into the Creek system was observed to be responsible for the contamination of Ebute Meta creek (Etim, 2012). Etim and Adie (2012) also observed that available sources of Potable water for drinking and industrial chores in Nigeria are dwindling because of concomitant increase in population, urbanization and industrial activities.

Modern agriculture is now becoming a nuisance to mankind. The insecticides, pesticides, chemical fertilizers especially nitrate and phosphate are used annually to boost agricultural production and these chemicals are washed down the soil by rain and eventually end up to contaminate the ground water and stream waterways and River Kubanni is equally surrounded by these types of activities which are likely to pollute the waterway. Several soil mining and quarrying activities are common in the Kubanni catchment area which may have similar effects on the aquatic lives. Most metals are known to be carcinogenic and fatal, they are generally dangerous to living organism especially man because of their bioaccumulation nature, they accumulate in living tissues anytime they are taken up and stored faster than they are metabolized or excreted (Leutech, 2006). Increased technology has lead to rapid industrialization and by implication increased pollutants in the environment and therefore exposes man to environmental risk. Environmental pollution is a big problem in modern society; out of the various kinds of pollution, the high contamination of aquatic systems with toxic heavy metals is of major concern since metals are no biodegradable and their elevated uptake by crops may affect food quality and safety (Barakat et al., (2012). The Kabanni River is prone to metal pollution by the intense anthropologenic activities within the catchment area. Therefore the aim of this study is to examine the levels of concentration of these metal pollutants in the entire Kubanni waterway and make necessary recommendations for abatement of further loading of these toxic chemicals into the water body and other water sources.

2. The study area

The study area is the Kubanni River basin in Zaria, Kaduna State Nigeria. The Kubanni River takes its source from the Kampagi hills in Shika near Zaria. It flows in southeast direction of Ahmadu Bello University Zaria. The Kubanni River flows southwards in a total length of 21km into River Galma (Lat 11^0 04'59.77"N - 11^0 08' 29.77N and Long $07^034'59.84"E - 07^041'59.84E$). The Kubanni catchment area belongs to the northeastern part of Kaduna River basin which borders the Chad basin. The Kubanni River was damned by the authorities of Ahmadu Bello University in 1973 at about 7.25km from source to provide water to the University Community (Iguisi, 2001). The Kubanni catchment area lies within the tropical wet and dry climatic zones, characterized by strong seasonality and temperature distribution.

The geology of the study area is composed mainly of fine grain gneisses and migmatite with some course-grained granitic outcrops in few places. The soil of the study area is mainly sandy-clay loan with poor infiltration because of the high clay content (Iguisi, 1997). Except for Aeolian, deposit and fadama soils, the soils of Kubanni basin are mainly derived from the basement complex and quaternary deposits. The Kubanni basin lies in natural vegetation zone known as the Northern Guinea Savanna and the entire vegetation and soils of the study area have been under great anthropogenic influences which have greatly modified the entire landscape.

3. Materials and method

3.1. Materials. The main sources of data for this study were sediments from four different sampling points along the long profile of Kubanni River channel that spanned to about 21km. The choice of the sediment for the study is because metals are known to be more concentrated in sediments than surface water (Rognerud and Fjeld, 1993). Sediment in aquatic environment serves as a pool that can retain and release metals to the water column by various methods of remobilization (Caccia *et al.*, 2003; Pekey, 2006 ; Marchand *et al.*, 2006) The long profile of the river was divided into the upper, middle and the lower courses and the sampling points were code named KP1 – KP4 as shown on Figure 1. The sediment samples were obtained at each sampling point along River Kubanni using sediment core made of polyethylene plastic with a column length of 1m.

3.2. Methodology. The sediments were acidified to suppress the growth of microorganisms. The sediments were prepared in the laboratory and analyzed, the certified reference materials IAEA –SL-3 (sediment) was used to determine the calibration factor for all the elements. The Instrumental Neutron Activation Analysis (INAA) technique was adopted in the analysis of the data using Nigeria Research Reactor -1 (NIRR -1) which is a miniature

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Neutron Source Reactor (MNSR). The NIRR-1 is a low power nuclear reactor which has proved to be the most accurate in analyzing metal concentrations in sediments (Jonah *et al.*, 2006).

To analyze the data, two irradiation schemes were adopted based on the half life of the product radionuclide, for elements leading to short lived activation product the prepared samples were irradiated in an outer irradiation channel B4, for elements leading to long lived activation products samples were irradiated for 6hr in the inner irradiaton channel. Following the short-lived irradiation regime the first round of counting was done for 10min (i.e. S1) after a waiting time of 2-5min. The second round of counting was carried out for 10min following the irradiation regime (i.e. S2) after a waiting period of 3-4hr.

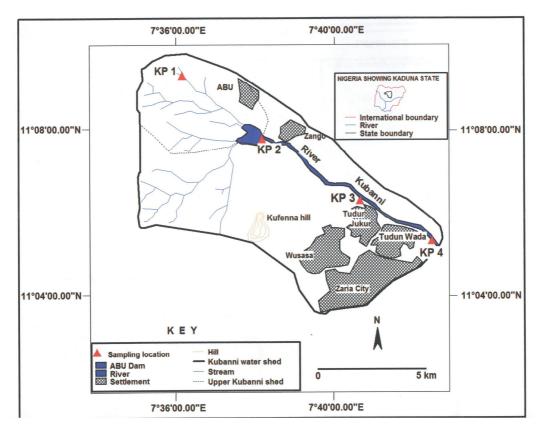


Figure 1: The study area showing the sampling locations (KP1 – KP4) Source: Nigeria SAT – 1 Imagery, 2009

In long irradiation regime the first counting was done for 30min, after a waiting time of 4-5 days and the second counting was carried out for 60min after a cooling time of 10-15 days. Finally, the identification of gamma-ray of product radio-nuclides through their energies and quantitative analysis of the concentration of each of the elements in the sample were obtained by using the gamma-ray spectrum analysis software, WINSPAN 2004. The results of the 8 samples that were collected in each location were summed up and their mean was taken to represent the concentration in that particular section of the river, then the entire data generated by laboratory analysis were summarized by simple descriptive statistics such as mean, standard deviation and coefficient of variation.

4. Results and discussion

The results of the laboratory analysis as shown on Table 1 indicated the presence of 29 metal pollutants; Mg, Al, Ca, Ti, V, Mn, Dy, Na, K, As, Br, La, Sm, V, U, Sc, Cr, Fe, Co, Zn, Rb, Cs, Ba, Eu, Lu, Hf, Ta, Sb and Th in River Kubanni at different levels of concentration. The maximun concentration of Mg is 4000 ppm, minimun is 2000 ppm and the mean concentration in the stream is 2750 ppm. Al has maximum concentration of 42000 ppm, the minimun concentration is 35000 ppm and the mean concentration in the river is 4000 ppm. The maximum concentration of Ca is 8000 ppm, minimun is 1000 ppm and mean concentration is 4250 ppm with 77% cofficient of variation (CV). The maximum concentration of Ti is 2000 ppm, minimum is 2000 ppm and the mean value is 35.3 ppm. The maximum concentration of Mn in the river is 247.8 ppm with maximum value of 293.3 ppm and minimum concentration of 184.5 ppm.Dy has low level of concentration in River Kubanni, the mean value is 6.3 ppm, maximum concentration is 7.3 ppm and minimum is 4.7 ppm.

The mean concentration of Na is 2000 ppm, maximum and minimum concentration during the sampling period is 2000 ppm. The maximum concentration of K is 21000 ppm, minimum value is 2000 ppm and the mean concentration in the stream is 15500.0 ppm, with high standard deviation of 9110.4. The mean value of As is 1.8 ppm, maximum is 3.7ppm and minimum is 1.2 ppm and the coefficient of variation (CV) is 58.8%. The mean concentration of Br in the river is 1.0 ppm, maximum is 2.2 ppm and minimum is 0.4ppm with CV of 85.1%.

The maximum level of concentration of La is 51.3ppm, minimum concentration is 28.5ppm and mean concentration is 37.5 ppm. The mean concentration of Sm is 29.6 ppm, the maximum concentration is 53.00 ppm and the minimum is 6.7 ppm while the CV is 77%. The mean concentration of Yb is 5.9 ppm and the maximum concentration is 6.7ppm. The maximum concentration of U is 5.8 ppm, minimum is 5.4 ppm and mean concentration is 5.4 ppm.

Sc mean level of concentration is 3.8 ppm, Cr is 18.4 ppm, Fe has high mean concentration of 16500 ppm, with high maximun level of 19000 ppm and minimum level 15000 ppm during the sampling period. The mean concentration of Co is 4.2 ppm, Zn is 103.7 ppm with a wide range of 174.6 and Cv of 72.7%. Rb mean value is 121.7 ppm, Cs is 3.7 ppm,Ba is 402 ppm with high maximum concentration of 489.6 ppm in KP1. The mean concentration of Ta is 2.1 ppm, Lu is 0.7 ppm, Hf is 19.9 ppm with highest concentration of Sb is 1.4 ppm, maximum concentration of 2.3 ppm in KP2. The mean concentration of Sb is 1.4 ppm, maximum concentration of 1.8 ppm in KP2 with high CV of 73.9%. Finally Th has mean concentration of 21.4ppm with maximum concentration in KP4 (29.3 ppm) and minimum concentration in KP1 (17.4 ppm).

Table 1 The levels of concentration of metal contaminants in the entire river Kubanni (kP1-4)

ELEMENT	MEAN	MEAN	MEA	MEA	MAX	MIN	MEA	SD	CV
(PPM)	KP1	KP2	N KP3	N KP4			Ν		
Magnesium Mg	4000.0	2000.0	3000.0	2000.0	4000.0	2000.0	2750.0	957.43	34.8%
Aluminium Al	42000.0	35000.0	45000.	38000.	45000.	35000.	40000.	4396.9	11.0%
Calcium Ca	8000.0	1000.0	6000.0	2000.0	8000.0	1000.0	4250.0	3304.0	77.7%
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Titanium Ti	2000.0	3000.0	4000.0	3000.0	4000.0	2000.0	3000.0	816.50	27.2%
Vanadium V	33.6	41.1	36.1	30.5	41.1	30.5	35.3	4.49	12.7%
Manganese Mn	293.3	287.5	225.8	184.5	293.3	184.5	247.8	52.07	21.0%
Dyspiosium Dy	6.1	4.7	7.3	7.3	7.3	4.7	6.3	1.23	19.4%
Sodium Na	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	2000.0	0.00	0.0%
Potassium K	2000.0	21000.0	18000.	21000.	21000.	2000.0	15500.	9110.4	58.8%
Arsenic As	1.8	1.2	3.7	1.4	3.7	1.2	2.0	1.14	56.4%
Bromine Br	0.8	0.5	2.2	0.4	2.2	0.4	1.0	0.84	85.1%
Lanthanium La	33.4	28.5	36.8	51.3	51.3	28.5	37.5	9.83	26.2%
Samarium Sm	6.7	45.3	53.0	13.5	53.0	6.7	29.6	22.92	77.3%
Yittarbium Yb	6.7	4.5	6.0	6.3	6.7	4.5	5.9	0.98	16.8%
Uranium U	5.4	5.4	5.4	5.8	5.8	5.4	5.5	0.20	3.6%
Scadium Sc	3.8	2.5	4.2	4.1	4.2	2.5	3.6	0.78	21.5%
Chromium Cr	18.4	21.3	29.3	28.3	29.3	18.4	24.3	5.30	21.8%
Iron Fe	16000.0	16000.0	19000.	15000.	19000.	15000.	16500.	1732.0	10.5%
Cobalt Co	4.8	3.4	4.5	4.0	4.8	3.4	4.2	0.62	15.0%
Zinc Zn	71.4	35.4	210.0	97.8	210.0	35.4	103.7	75.37	72.7%
Rubidium Rb	147.6	100.6	108.3	130.4	147.6	100.6	121.7	21.39	17.6%
Caesium Cs	6.1	2.0	3.4	3.3	6.1	2.0	3.7	1.73	46.7%
Barium Ba	489.6	373.1	342.3	403.3	489.6	342.3	402.1	63.47	15.8%
Europium Eu	1.0	0.7	0.8	0.9	1.0	0.7	0.8	0.12	14.4%
Lutetium Lu	0.8	0.5	0.6	0.7	0.8	0.5	0.7	0.12	18.1%
Hafnium Hf	15.7	15.8	19.0	25.0	25.0	15.7	19.9	4.70	23.6%
Tantanium Ta	1.8	2.3	2.2	1.9	2.3	1.8	2.1	0.25	12.2%
Antiniony Sb	2.3	0.2	2.1	0.8	2.3	0.2	1.4	1.01	73.9%
Thorium Th	17.4	17.8	21.4	29.3	29.3	17.4	21.4	5.52	25.7%

A total of 29 metal pollutants were identified in each of the sampling points in entire Kubanni River, however the levels of concentration of each of the metal pollutants differ from one sampling point to another. This is because of the peculiarity of the human activities in each of the four sampling points. Barakat *et al.*, (2012) observed that higher degree of metal pollution was at sampling stations close to Beni-Mellal city, Morocco, which confirms that the major sources of heavy metal were from industrial and urban waste water discharge, also relatively high heavy metal contamination at stations close to rural areas suggested that agricultural and rural activities carried out at the wide lands surrounding the Day River might have attributed to metal pollution in the river sediment. The presence of each of the metal pollutants in the entire river is a reflective of the manner in which turbulence flows within the river and indeed the effect of stream flow can thoroughly mix-up the river water to the extent of ensuring spatial uniformity in the levels of concentration of these metal contaminants. The cause of the observed variation in the levels of concentration which are readily detached and entrained by overland flow tend to exhibit higher levels of concentration while those that are gradually released from the soil regolith system through subsurface and base flow show lower levels.

Metal pollutants such as Al, Mn, Ca, K, Fe, As and Sc whose sources are traceable to refuse dumps, farmlands public gutter and effluents from research centres and institutions in the catchment area exhibited higher levels of concentration in River Kubanni than those whose sources are restricted to weathered rocks and perhaps other sources where they occur at very low concentration, example Ta, Rb, Yb Dy, As, Br, U, Eu and Lu). These variations are

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therefore, the reflection of the relative abundance of these metal pollutants in the catchment area of River Kubanni and the ease with which overland, surface and base flow transport them into the river.

4. Recommendations

Water is one of the most important natural resources without which life on earth will be impossible; this therefore justifies the need for proper management and protection of available water sources from contamination by chemical pollutants. It is therefore recommended that:

a. Indiscriminate dumping of refuse which litter the built up area of the Kubanni catchment area should be discouraged.

b. The ugly practices such as discharging of oils petrol, used batteries, grease, training effluents and salon effluents into public drains which finally end up into the river should be discouraged.

c. The use of toxic chemicals for farming should be controlled.

d. Our towns and cities should have a simple and effective sewage treatment. Sewage should not be discharged into public drains or water bodies.

e. Government should provide necessary vehicles for regular evacuation of all the refuse dumps that are commonly seen in our cities.

6. Conclusion

The study has established that 29 different types of metal contaminants; Mg, Al, Ca, Ti, V, Mn, Dy, Na, K, As, Br, La, Sm, Yb, U, Sc, Cr, Fe, Co, Zn, Rb, Cs, Ba, Eu, Lu, Hg, Ta, Sb, and Th exist in River Kubanni at different levels of concentration. It is expected that the levels of concentration of these metal pollutants will continue to increase, since most of the metal sources are from human activities that are on daily increase in the catchment area. The contaminations of the waterway by these metal pollutants may have direct consequences on the lives of the consumers on the long run because metals are known to be carcinogenic to humans.

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Ali Williams Butu hails from Takum, Taraba state, northeast Nigeria. He received a B.Sc.(1990), M.Sc.(2002), PhD(2011) Degrees in Geography from Ahmadu Bello University Zaria, Nigeria. He also holds a Postgraduate Diploma in Education (PGDE) from the famous Tai Solarin University of Education Ijagun, Ogun state, southwest Nigeria. His field of study is Hydrology and water resources management. He has written several articles on water pollution by metal contaminants.