

Spatial Variation in the Levels of Concentration of Metal Contaminants in River Kubanni Zaria, Nigeria.

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Abstract

The paper looked at the spatial variation in the levels of concentration of metal contaminants in river Kubanni Zaria, Nigeria. The main sources of data for the study were sediments from four different sections of the long profile of the river and the instrumental Nitrogen Activation Analysis (INAA) technique was adopted in the analysis using Nigeria Research Reactor-1 (NIRR-1). The NIRR-1 is a miniature Neutron Source Reactor (MNSR). The chemical contaminants, Mg, Al, Ca, Ti, V, Mn, Dy, Na, K, As, La, Sm, Yb, U, Br, Sc, Cr, Fe, Co, Rb, Zn, Cs, Ba, Eu, Lu, Hf, Ta, Sb, and Th currently exist in all the sections of the river in different levels. The statistical inference from ANOVA and student f-test shows that there is no significant difference in the levels of concentration of the metal pollutants between one section of the river (sampling point) and another. This is therefore a reflection of the manner in which turbulent flow 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 level of concentration of these metal contaminants

Keywords: Catchment area, levels of concentration, metal contaminants, river Kubanni sediment, significant difference, spatial variation.

1. Introduction

The rate of water pollution of all types has increased much more as compared to other fields of pollution due to discharge of all sorts of obnoxious matter into it (Akhtar, et al., 2005). Adakole and Abolude (2012) observe that global concern about heavy metals in the environment stems from their persistence, toxicity and bioaccumulation in the trophic chain. When heavy metals enter water bodies they change water quality, bind to sediment and accumulate in aquatic biota causing anemia, disturbance of physiological functions and mortalities of fish (Post, 1983). Metal contaminants also pose serious threat to humans through ingestion of metal enriched aquatic organisms.

Amman, *et al* (2002) are of the view that anthropogenic activities like mining, final disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates from different industries, such as tannery, steel plants, battery, industries, thermal power plants and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture are some of the main causes of metal pollution in the aquatic ecosystem. Although some metals like Cu, Fe, Mn, Ni, Zn and Se are essential micronutrients for life processes in plants and animals, others like Cd, Cr, and Pb have no physiological activity and have been proven detrimental beyond certain limit (Marschner, 1995; Bruins, *et al.*, 2000). Trace elements constitute a natural component of the earth crust and are not biodegradable, hence persist in the environment. Trace elements may come from natural sources, leached from rocks and soils according to their geochemical mobility or come from anthropogenic sources as a result of human land occupation and industrial pollution (Abolude, *et al.*, 2009).

The rate of increase in level of concentration of metal contaminants in domestic water is highly worrisome. Butu (2002) reported the presence of lead, chromium, iron and cobalt in significant concentration above WHO limit for domestic purpose in the Galma dam. Iguisi, *et al* (2001) reported the presence of heavy metals in Kubanni dam and further observes that several chemical elements in the dam have their origins from the decomposing high refuse dumps that dotted the landscape of the built up sections of the catchment area of Kubanni dam. Several other studies have shown that a considerable number of chemical elements are leached from refuse dumps during raining season into groundwater and streams (Farouk, 1987; Olofin, 1991). Yusuf (1993) observes that chlorine gas, zinc, copper, ammonia gas, hydrogen sulphide, sulphide dioxide, lead, iron and aluminium in large quantities were released into the soil profile in Kano Metropolis from refuse dumps. He observes that these chemical elements are continually leached out of these refuse dumps as overland flow, infiltration and percolation into groundwater and ultimately into rivers and dams.

Mechanical workshops where used engine oil and petrol are continually discarded are available sources of lead. Air pollution from exhaust pipes and incinerators have also been reported to be capable in the release of chemical pollutants into water bodies (Butu, 2002). Ewa, *et al* (1999) are of the view that animal superficial contamination from terrestrial runoff, Aeolian deposition from strong winds and storms from the Saharan desert emanating from the Air region in Niger Republic could account for the unusual deposition of uranium and

thorium in water sediments around the Sahel Savanna region. Lawal and Singh (1981) reported a high degree of environmental pollution that was caused through discharge of effluents into streams, sewage and on the land. The Kubanni basin is also dominated by human activities and it is possible that the Kubanni River could be polluted through these means. Dim, *et al* (2002) also examined the Kubanni River sediments and reported the presence of uranium and thorium enrichment. They suggested that the probable contributory factors for the enrichment of these metals in the river sediments are either from phosphate fertilizers used on the neighbouring farms or from deposition by the Northeast Trade winds across the northern Nigeria savannah region. Another major contributing source is the annual weathering of the basement granites. These activities are on daily increase and at different rates in different sections of the Kubanni catchment area. Consequently, it is expected that they may give rise to spatial concentration of these metal pollutants in river Kubanni which is the only major waterway in the basin.

The contamination of inland waterways is globally known to impact negatively on the environment. These inland water ways include lagoons, rivers, lakes and creeks, and are prominent hydrological features. One of such water ways which has found prominent in the cities of Kaduna State is the Kubanni River, Zaria. The proliferation of urban settlements and slums around the Kubanni River has also meant increased human pressure and the resultant deterioration of the water way. The Kubanni River originates from Kampangi hills and passes through several urban and rural settlements. The river receives domestic effluents, and industrial waste waters without any treatment directly from the Samaru, Ahmadu Bello University (ABU) Campus and the surrounding settlements. Further, waste waters from rural agglomerations also enter into this river. Because river Kubanni is often used for irrigating agricultural lands and is also dammed to provide domestic water for the ABU community and there is growing concerns about potential contamination in this area and the potential impact on food systems and human health. While there is strong evidence of pollution of this ecosystem, no investigation has been previously conducted to characterize metal contaminants in relation to their spatial variability in river Kubanni. Therefore, the aim of this study is to characterize the metal concentration in different sections of river Kubanni and to assess the spatial variation in the levels of concentration of these metal contaminants in the river.

2. The study area

The study area is the Kubanni River Zaria, Kaduna State Nigeria (Figure 1). The stream has its course from the Kampangi Hills near Shika. It flows southwards direction in a total length of about 21kms into the Galma River (Lat 11°04'59.77"N – 11°08'29.77"N and Long 07°34' 59.84"E – 07°41' 59.84"E). The Kubanni catchment area belongs to the Northeastern part of Kaduna River basin which borders the Chad Basin. It is located within the Central High Plains of Northern Nigeria Savannah region at approximately 670m above sea level (Yusuf, 1992).

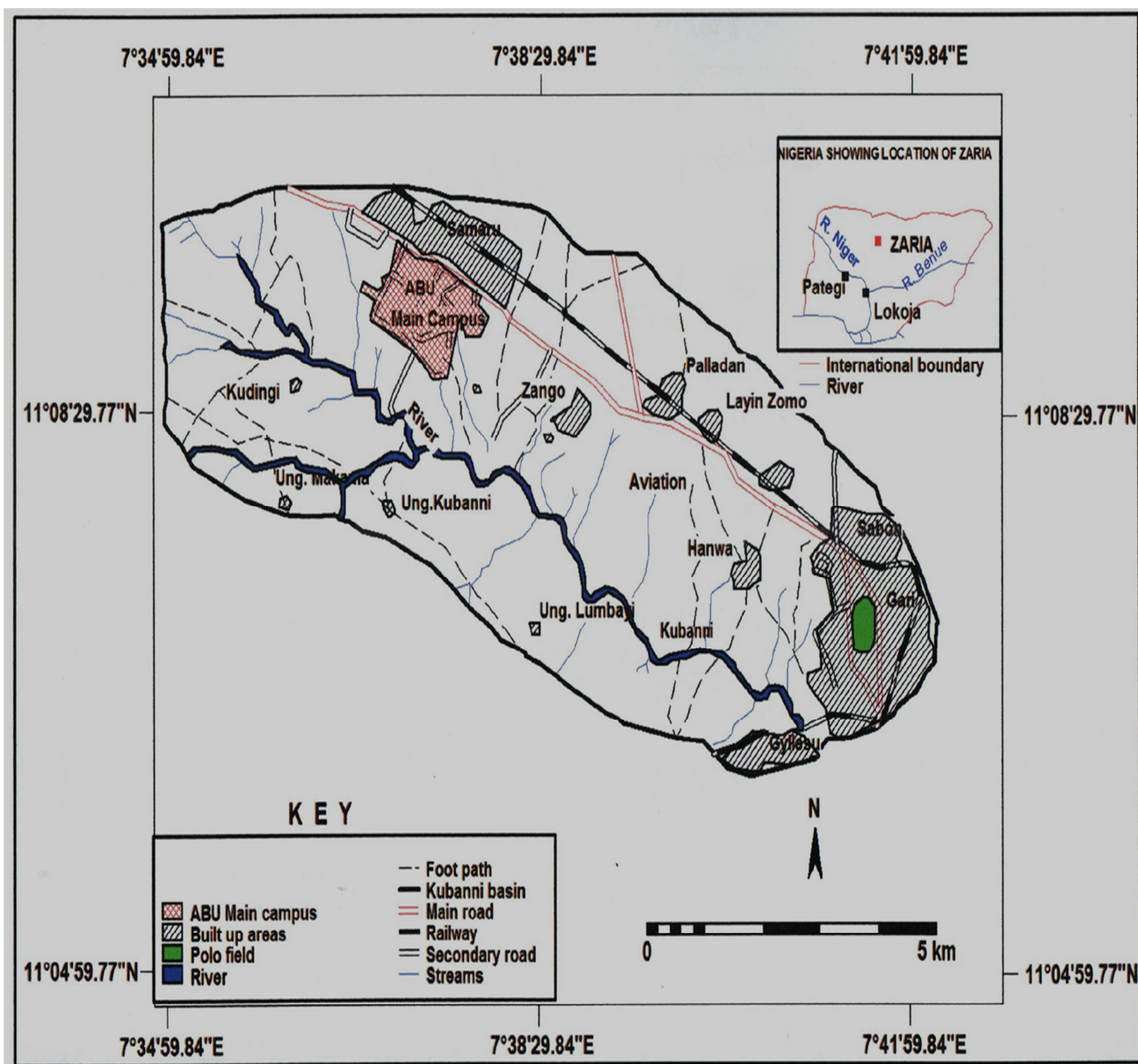


Figure 1: The Kubanni drainage basin

Source: Adopted from part of sheet 102 Zaria Sw

The Kubanni stream flows through several rural settlements and research institutions such as Ahmadu Bello University (ABU), Teaching Hospital, ABU main Campus, College of Agriculture Samarai, Centre for Energy Research and Training and Nigeria College of Aviation Technology as well as some urban settlements such as Zango, Palladan, Kwaugila, GRA, PZ, Tudun Jukun, Tundun Wada and Gyelesu. The Kubanni catchment area lies within the tropical wet and dry climatic zone characterized by strong seasonality and temperature distribution. The area experiences an average of six to seven raining months from March/April – October/November and five to six dry months from November to March.

The geology of the area is composed mainly of fine grain gneisses and migmatite with some grained granitic outcrops in few places. The depth of weathering is irregular but thorough; it ranges from 10m to deep pockets occasionally extending to about 60m (WAPDECO, 1991). The soil of the basin is classified as leached ferruginous tropical soil developed on regolith rich in fine grain quartz and oligoclass. The Kubanni River is one

of the tributaries of river Galma with its headwaters from Kampagi Hills and flows into river Galma near Gyelesu – Tudun Wada, Zaria. The Kubanni stream is a seasonal stream flowing at full capacity during the raining season with little surface water along stretches of the river channel in dry season. The Kubanni basin lies in guinea savannah vegetation zone but cultivation, bush burning and grazing activities have modified the natural vegetation cover and composition.

3. Materials and method

3.1 Sample collection and preparation. The main sources of data for this study are sediments from four different sampling points along the long profile of Kubanni River, Zaria Nigeria. The Kubanni River spans to about 21kilometres. The sediment samples for this study were collected from January to October 2008. The choice of sediment for this study is because metals are known to be more concentrated in sediments than surface water (Rognerad and Fjeld, 1993). Sediments in aquatic environment serve as pool that can retain and release metals to the water column by various methods of remobilization (Caccia, *et al.*, 2003; Pekey, 2006; Machard, *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 (Figure 2).

The sediment samples were obtained at each sampling points along river Kubanni using sediment core made of polyethylene plastic with a column length of one meter. 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.

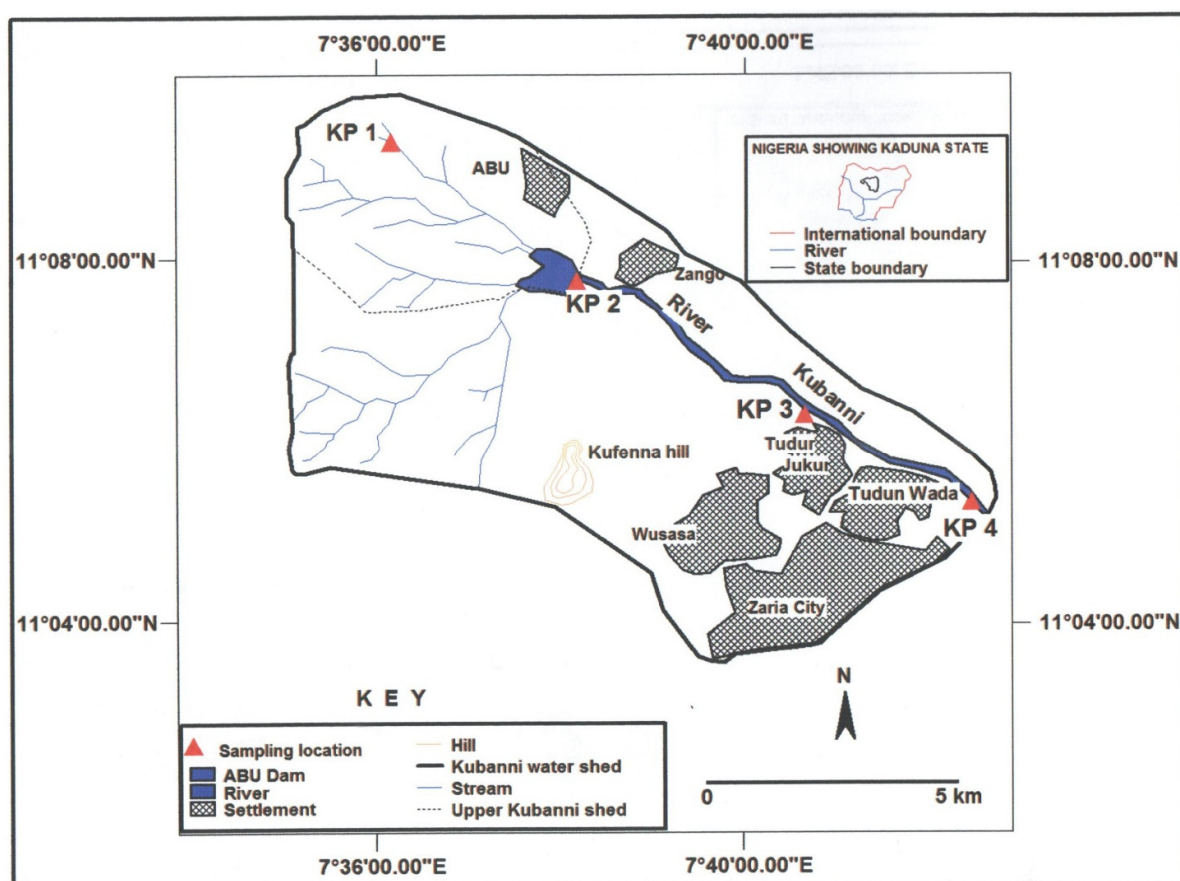


Figure 2. The study area showing the sampling locations (KP1 – KP4)

Source: Nigeria SAT – 1 Imagery, 2009

3.2. Laboratory technique: The instrumental Nitrogen Activation Analysis technique (INAA) was adopted in the analysis of the data using Nigeria Research Reactor – 1 (NIRR - 1). The Nigeria Research Reactor – 1

(INIRR - 1) is a Miniature Neutron Source Reactor (MNSR). It is specifically used for Nitrogen Activation Analysis (NAA) technique. NIIR – 1 is a low power nuclear reactor, which has highly enriched uranium as fuel, light water as moderator and beryllium as reflector. The associated facility for radioactivity measurement is a gamma-ray data acquisition system. It consists of a horizontal dip-stick Highly – Purity Germanium (HPGe) detector with a relative efficiency of 2% at 1332.5keV gamma-ray line, the MAETRO emulation software compatible with the ADCAM multi channel analyzer (MCA) card, associated electronic modules all made by EG & G ORTC and a personal computer. The NIIR-1 has proved to be the most accurate in analyzing metal concentration in sediments (Jonah, et al., 2006).

3.3. Laboratory Analysis: To analyze this data, two irradiation schemes were adopted based on the half life of the product radionuclide. For elements leading to short-lived activation products, the prepared samples were each packed and sealed in 7cm² rabbit capsules and irradiated in an outer irradiation channel B₄, where the nuclear spectrum is soft. The choice of the out irradiation channel is to eliminate corrections due to nuclear interferences of some elements because of proximity of the inner channels of the MNSR to Cole leading relatively higher ratio of fast to thermal neutrons.

For elements leading to long-lived activation products, samples were irradiated for 6 hours in the inner irradiation channels. The neutron flux variability over irradiation volume was determined experimentally to be less than 2% through measured specific activities of irradiated Cu wires arranged axially and radially inside the vial. The stability of neutron flux throughout the period of irradiation especially for long irradiation was checked by monitoring the neutron flux of reading of fission chamber connected to the Micro-computer control system. Radioactivity measurement of induced radionuclide was performed by the PC- based gamma-ray spectrometry. Following the short-lived irradiation regime the first round of counting was done for 10 mins (i.e. S1) after a waiting time of 2-5 mins. Samples were placed on a plexi-glass sample holder designated as “H2” which corresponds to source-detector geometry of 5cm. The second round of counting was also carried out for 10mins following the short-irradiation regime (i.e. S2) after a waiting period of 3-4 hrs. Samples were then counted on a flexi-glass holder designated as “H1” corresponding to a source-detector geometry of 1 cm.

In the long irradiation regime, the first counting was carried out for 30 minutes, following the long irradiation (i.e. L1) using the holder “H1” after a waiting time of 4-5 days. The second round of counting was performed for 60 mins (i.e. L2) after a cooling time of 10 – 15 days. Samples were counted using the flexi-glass holder “H1”. The choice of cooling time and sample-detector dead time was controlled to be less than 10%. Finally, the identification of gamma-ray of product radio-nuclides through their energies and quantitative analysis of their concentrations were obtained by using the gamma-ray spectrum analysis software, WINSPAN 2004.

4. Results and discussion

Table 1 show that the level of concentration of Mg in Kubanni River in Kampagi hills area (KP1) is 33800.0ppm, in Kubanni dam (KP2) is 2200.0ppm, in KP3 around Palladan Bridge is 2000.0ppm and KP4 in Gyelesu area is 2100.0ppm. The level of concentration of Al in KP1 is 42200.0ppm, 34900.0ppm in KP2, 452400.0ppm in KP3 and 37800.00.0ppm in KP4. In KP1, the level of concentration of Ca is 7900.0ppm, 1400.0ppm in KP2, 3900.0ppm in KP3 and 1700.0ppm, in KP4. Ti level of concentration in river Kubanni in PK1 is 2100.0ppm, 22700.0ppm in KP2 with standard deviation (SD) of 0.11, in KP3 the mean concentration is 3500.0ppm with standard deviation of 0.06 and in KP4 the level of concentration of Ti is 3200.0ppm with SD of 0.11. In KP1, the level of concentration is of V is 33.63ppm with SD of 26.76, in KP3 the mean concentration is 17.21ppm and in KP4 the mean concentration is 30.50ppm with SD of 10.38.

In KP1, the mean level of concentration of Mn is 293.25ppm with SD 135.21, the level concentration in KP2 is 41.13ppm the value in KP3 is 225.75ppm with SD of 71.21 and the mean concentration in KP4 is 30.50ppm with SD of 10.38. In KP1, the level of concentration of Dy is 6.10 with SD of 1.87, in KP2 the mean concentration is 7.29ppm and 7.28ppm with SD of 2.79 in KP4. Na has mean concentration of

<i>ELEMENT/ METALS</i>		<i>KP 1</i>		<i>KP 2</i>		<i>KP 3</i>		<i>KP 4</i>	
		<i>MEAN</i>	<i>SD</i>	<i>MEAN</i>	<i>SD</i>	<i>MEAN</i>	<i>SD</i>	<i>MEAN</i>	<i>SD</i>
<i>Magnesium</i>	<i>Mg ppm</i>	3800.00	0.10	2200.00	0.06	3000.00	0.09	2100.00	0.07
<i>Aluminium</i>	<i>Al ppm</i>	42200.00	1.90	34900.00	0.64	45400.00	2.09	37800.00	1.31
<i>Calcium</i>	<i>Ca ppm</i>	7900.00	1.05	1400.00	0.04	5900.00	0.64	1700.00	0.05
<i>Titanium</i>	<i>Ti ppm</i>	2100.00	0.11	2700.00	0.11	3500.00	0.06	3200.00	0.13
<i>Vanadium</i>	<i>V ppm</i>	33.63	10.72	41.13	26.76	36.14	17.21	30.50	10.38
<i>Manganese</i>	<i>Mn ppm</i>	293.25	135.21	287.50	74.70	225.75	71.78	184.50	59.75
<i>Dysprosium</i>	<i>Dy ppm</i>	6.10	1.87	4.70	1.25	7.29	2.25	7.28	2.79
<i>Sodium</i>	<i>Na ppm</i>	2300.00	0.10	1700.00	0.05	2300.00	0.09	1900.00	0.04
<i>Potassium</i>	<i>K ppm</i>	20100.00	0.42	20600.00	0.62	17600.00	0.84	21300.00	0.35
<i>Arsenic</i>	<i>As ppm</i>	1.83	0.82	1.19	0.57	3.69	5.31	1.40	0.57
<i>Bromine</i>	<i>Br ppm</i>	0.78	0.66	0.49	0.21	2.22	2.74	0.45	0.09
<i>Lanthanium</i>	<i>La ppm</i>	33.44	11.15	28.49	13.48	36.78	15.05	51.34	23.65
<i>Samarium</i>	<i>Sm ppm</i>	6.74	1.34	45.32	111.9	53.0	130.1	13.51	14.57
<i>Ytterbium</i>	<i>Yb ppm</i>	6.70	2.77	4.45	4.58	5.98	3.68	6.30	5.69
<i>Uranium</i>	<i>U ppm</i>	5.35	0.95	5.40	3.40	5.44	2.99	5.79	1.39
<i>Scandium</i>	<i>Sc ppm</i>	3.78	1.24	2.50	0.94	4.20	2.11	4.09	1.31
<i>Chromium</i>	<i>Cr ppm</i>	18.38	7.93	21.30	4.64	29.25	13.78	28.25	10.38
<i>Iron</i>	<i>Fe ppm</i>	16300.00	0.47	15600.00	0.36	18900.00	0.70	15400.00	0.47
<i>Cobalt</i>	<i>Co ppm</i>	4.80	1.42	3.36	1.45	4.49	2.06	4.03	0.80
<i>Zinc</i>	<i>Zn ppm</i>	71.40	86.75	35.40	19.39	210.0	171.4	97.83	73.03
<i>Rubidium</i>	<i>Rb ppm</i>	147.63	44.59	100.63	23.49	108.25	44.58	130.38	26.33
<i>Caesium</i>	<i>Cs ppm</i>	6.14	3.40	2.03	0.58	3.43	1.05	3.25	1.81
<i>Barium</i>	<i>Ba ppm</i>	489.63	115.08	373.13	114.6	342.25	162.6	403.25	183
<i>Europium</i>	<i>Eu ppm</i>	0.96	0.26	0.67	0.22	0.83	0.23	0.87	0.23
<i>Lutetium</i>	<i>Lu ppm</i>	0.82	0.32	0.55	0.63	0.61	0.32	0.74	0.52
<i>Hafnium</i>	<i>Hf ppm</i>	15.68	9.73	15.78	5.23	19.01	9.39	25.04	12.94
<i>Tantalum</i>	<i>Ta ppm</i>	1.78	0.41	2.32	1.27	2.21	0.80	1.92	0.52
<i>Antimony</i>	<i>Sb ppm</i>	2.34	3.35	0.25	0.11	2.07	2.89	0.79	0.71
<i>Thorium</i>	<i>Th ppm</i>	17.35	7.20	17.75	11.08	21.40	9.14	29.25	13.95

Table 1. Comparison of the levels of concentration of metal pollutants between each section of the river (kp) and another

Source: Field Survey, 2008.

2300.0ppm in KP1, 1700.0ppm in KP2, 2300.0ppm in KP3 and 1900.0ppm in KP4. The mean concentration of K in KP1 the Kampangi Hills area is 20100.0ppm, 20600.0ppm in KP2 ABU dam area, 17600.0ppm in KP3 and 21300.0ppm in kp4 Gyelesu area. The level of concentration of As is KP1 is 1.83ppm, the mean concentration in KP2 the ABU dam is 1.19ppm, the mean concentration in KP3 the Palladan bridge area is 23.69ppm 1.40ppm Gyelesu area (KP4).

The mean concentration of Br in Kampangi Hills (KP1) is 0.78ppm, the mean concentration in KP2 is 0.49ppm, the mean concentration in KP3 is 2.22ppm and the concentration in Gyelesu area (KP4) is 0.45ppm, La has mean concentration of 33.44ppm in KP1, the mean value in ABU dam is 28.49ppm, the concentration in KP3 is 36.78ppm and the level of concentration in KP4 is 51.34ppm. The level of concentration of Sm in KP1 is 6.74 ppm, in Kp2 the concentration is 45.32ppm, in KP3 the value is 53.0ppm and 13.51ppm in KP4. The mean concentration of Yb in KP1 is 6.70ppm, the value in KP2 is 45.32ppm, in KP3 the mean concentration is 5.98ppm and 6.30ppm in KP4. The mean concentration of U is Kampangi Hills (KP1) is 5.35ppm, 4.45ppm in KP2 (ABU dam), 5.44ppm in KP3 and 5.79ppm in KP4. The level of concentration of Sc in KP1 is 3.78ppm, 2.50ppm in KP2, 4.20ppm in KP3 and 4.09ppm in KP4. The mean concentration of Cr in KP1 is 18.38ppm, 21.3ppm in KP2, 29.25ppm in KP3 and 28.25ppm. The level of concentration of Fe is 16300.0ppm in KP1 15600.0ppm in ABU dam (KP2), 18900.0ppm in KP3 and 15400.0ppm in KP4 Gyelesu area.

Fe has the highest level of concentration in the entire river. The mean concentration of Co in KP1 is 4.80ppm, 3.38ppm in KP2, 4.49ppm in KP3 and 4.03ppm in KP4. Zn has mean concentration of 71.40ppm in KP1, 35.40ppm in KP2, 210.0ppm in KP3 and 130.38ppm in KP4. The mean concentration value of Cs in Kampangi Hills (KP1) is 6.14, 2.03ppm in ABU dam, 4.43ppm in KP3 and 3.25ppm in KP4, Gyelesu area.

Ba has high level of concentration in the Kubanni stream, the value in KP1 is 489.63ppm, 373.13ppm in KP2, 342.25ppm in KP3 and 403.25ppm in KP4. Eu level of concentration in KP1 is 0.96ppm, 0.67ppm in KP2, 0.83ppm in KP3 and 0.87ppm in KP4. The table shows that the mean concentration of LU in KP1 is 0.82ppm; the concentration in KP2 is 0.55ppm, 0.61ppm in KP3 and 0.74ppm in KP4. Hf has mean concentration of 15.68ppm in KP1, 15.78ppm in KP2, 19.01ppm in KP3 and 25.04ppm in KP4. The value of Ta in KP1 is 1.78ppm, 2.32ppm in KP2, 2.21ppm in KP3 and 1.92ppm in KP4. The level of concentration of Sb in Kampangi Hills (KP1) is 2.34ppm, 0.25ppm in KP4 (ABU dam), 2,89ppm in KP3 and 0.79ppm in KP4 (Gyelesu area). Finally the level of concentration of Th in KP1 is 17.35ppm, 17.75ppm, KP2 21.40ppm in Kp3 and 29.25ppm in Kp 4 around Gyelesu area with very low standard deviation in each of the sampling points.

Table 2: ANOVA

Sources of Variation	Sum of Square (SSb)	Degree of Freedom (df)	Mean of Square (msb)	Fraction (F cal)	F = Critical (F tab)
Between Group Treatment	688.50	3	229.50	0.10	2.68
Within Group Treatment	891661.68	112	7961.27	0.10	2.88

Treatment at 0.05%, Level = 2.68

4.1. Decision: Since F_{cal} is less than F_{tab} ($0.10 < 2.68$): We do not reject H_0 ; hence there is evidence to show that there is no significance difference between the levels of concentration of pollutants between different sections of rive Kubanni Zaria, Nigeria.

Table 1 show that 29 metal contaminants exist in river Kubanni. The levels of concentration of these metals differ slightly in each section of the river (sampling locations, KP1-4). From Table 2, the statistical inference shows that there is no significant evidence to show that there is significant difference between the levels of concentration of metal pollutants between one section of the river (KP1) and another as proved by the student f-test. This is therefore a reflective of the manner in which turbulent flow 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 levels of concentration of these metal contaminants in river Kubanni.

The reason for the simple observed variations in the levels of concentration of these metal pollutants in each of the sampling locations is traceable to their various sources. Obviously metals pollutants 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. Chemical elements whose sources are traceable to refuse dumps, farmlands, public gutters and effluents from various research institutions and vast agricultural land 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 concentrations. These variations are therefore the reflection of the relative abundance of these chemical contaminants in the catchment area of river Kubanni and the ease with which overland, surface and base flow transport them into the river, but there is spatial variation in the levels of concentration of these elements in entire river Kubanni.

5. Conclusion

The study assessed the spatial variability of metal pollutants in river Kubanni, Zaria. It is observed that 29 metal pollutants exist in each of the four selected sampling points which represent different zones or sections of river Kubanni. Metals are known to be carcinogenic to humans when consumed in excess over a long period. The study shows that anthropogenic activities are the major contributing sources of metal pollutants in entire Kubanni water way. Debris transported into the stream during storm runoffs and metal contaminants that are leached into the soil and are also transported into the river through subsurface flow during the raining period. Metals released into the soil from the regolith system also contribute to the loading of contaminants in the entire Kubanni water course. The statistical inference shows that there is no significance evidence to show that there is significance difference in the levels of concentration of the metal pollutants in the different sections of the Kubanni stream. This is therefore a reflection of the manner in which turbulent flow within the river and indeed the effect of stream flow can thoroughly mix up the Kubanni channel water to the extent of ensuring spatial uniformity of the metal pollutants in the stream.

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