A Study on Heavy Metals Pollution Levels in Water and Sediment of River Kubani Dam, Zaria, Nigeria

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ABSTRACT

The study assessed the level of heavy metals (As, Cr, Pb, Cd, and Zn) in water and sediment of River Kubanni Dam. The heavy metals were determined using Microwave Plasma Atomic Emission Spectrophotometer (MPAES) model 4200. Concentration of metals in the sediment was higher compared to water. Metal concentrations in the sediment and in the water correlated positively except Cr and Pb. Concentration (mg/L) range for As (0.890 – 1.620) Cr (0.07 – 0.090) Pb (1.320 – 1.890), and Cd (0.078 – 0.098) in the water were higher than the World Health Organization (WHO) Permissible limit. Cd concentration range (4.43 – 7.230 mg/kg) in the sediment was above the United State Environmental Protection Agency (USEPA) standard, average shale value (ASV), toxicity reference value (TRV) and threshold effect level (TEL). Heavy metal pollution index (HPI) and metal index (MI) show that the river water was polluted; Geo-accumulation index (Igeo) indicated that the sediment was polluted only by Cd. Control of waste dumping and discharge of wastewater is required to prevent further pollution.

(Key words: heavy metals, concentration, metal indices, water, sediment, Pollution)

INTRODUCTION

High contamination of water environment with toxic heavy metals is of major concern since these metals are non-biodegradable and may eventually enter food chain leading to bioaccumulation in the body of human and posing threat to health (Suman, *et al*., 2018; Ogunwale, *et al*., 2020; Yan, *et al*., 2020). Heavy metals enter water systems mainly through natural sources such as weathering, run-off, and erosion of rock; and anthropogenic sources like industrial, agricultural and sewage disposal activities (Cevik, *et al.*, 2009; Adelekan and Abegunde, 2011).

Järup (2003) referred to metals with specific gravity greater than 5 g/cm^3 as heavy metals. Though some heavy metals such as Cu, Fe, Mn, Ni, Zn, Mo, Co, and Se are essential micronutrients, others like Cd, Cr, Hg, and Pb are not and have been proven to be detrimental beyond a certain limit (Bruins, *et al*., 2000; Oladebeye, 2017; Sandeep, *et al*., 2019). Deadly diseases like edema of eyelids, tumor, malfunctioning of genetic makeup, among others have been documented (Tsuji and Karagatzides, 2001).

Heavy metals in water bodies such as river Dam have the tendency to settle down to the bottom of the water and consequently trapped within the dam sediment by processes of adsorption, flocculation, and co-precipitation (Barakat, *et al.,* 2012). Thus, the underlying sediments in Dams and other water systems serve as a matrix that can retain metals or release sediment-bound metals to the overlying waters thereby bringing adverse effect to aquatic lives (Caccia, *et al*., 2003; Wang, *et al*., 2012).

The analysis of water, sediments, and aquatic organisms gives an estimation of the level of heavy metal contamination of an aquatic system, this is mainly justified especially where the water is used for irrigation in agriculture, filling of fishponds, water supply for households, industries, among others (El-Nemr, *et al*., 2012; Rzętała, 2016), this is the case for River Kubani Dam. Human activities around Ahmadu Bello

University, Zaria, and Samaru community, which are the immediate communities to River Kubani Dam, do not seem to decline but rather increase, hence, the Dam is under the threat of being steadily polluted with heavy metals (Ekwuribe, *et al*., 2016). This paper therefore assessed heavy metal pollution level in water and sediment of River Kubani Dam, to evaluate the pollution level of these metals by comparing their concentration levels to stipulated standards and metal indices.

MATERIALS AND METHODS

<u>Study Area</u>

River Kubanni dam, which is prevalently called Ahmadu Bello University (ABU) dam is located approximately within latitude 11°11'N and longitude 7°38'E, it is within the premises of the University main campus (Butu and Ati, 2013). The Dam was constructed in 1973 to supply water to ABU community with a catchment's area of 57 Km^2 (22 square miles), its width is 122 m (400 feet), mean depth is 6 m (20 feet) (Adakole and Abolude, 2012). It has a length of 800 meters and a concrete section of 10.36 meters above the riverbed (Ologe, 1973; Ekwuribe 2016).

Metal pollutants of the Dam and their sources are traceable to refuse dumps, farmlands and public drains, and this could increase heavy metal concentration in the Dam (Butu and Ati, 2013). River Kubani Dam is a fishing ground and fishing is carried out on daily basis, it also serves as a source of water for irrigation as its basin is a booming crop farming Area (Udiba *etal.,* 2013).

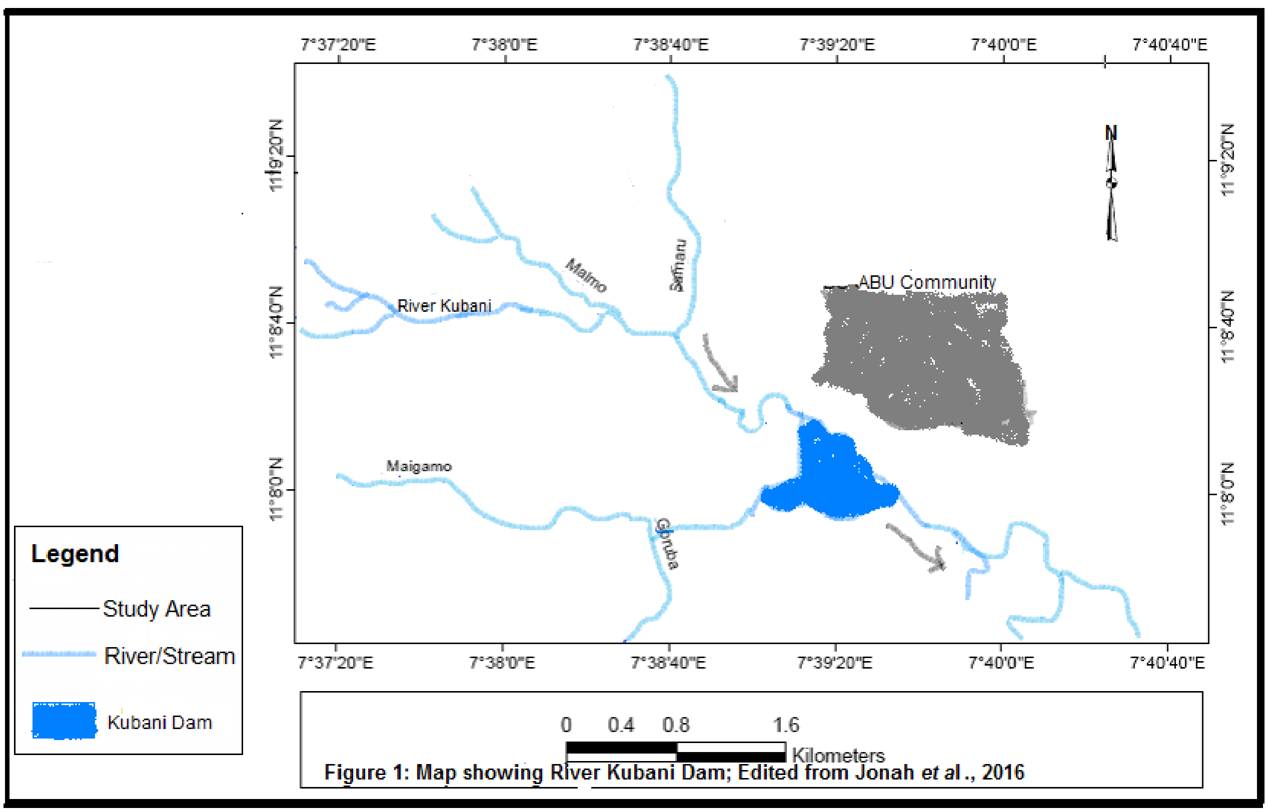

Figure 1: Study Area.

Sample Collection and Analysis

The Dam profile was divided into upper and lower part, four (4) sampling Sites were chosen, two (2) in the upper part and another two (2) in the lower part. Water Samples were collected using airtight 1 litre polyethylene plastic (high-density) bottles at interval of fifty meters, the collection was done at a depth of 20 – 40 cm. Sample bottles were washed thoroughly with solution of detergent and rinsed with deionized water. Then soaked in 10% "Analar" nitric acid (HNO_3) overnight followed by rinsing with deionized water to remove trace elements contamination according to Wufem, *et al*. (2009) and Abah, *et al*. (2016).

The sample bottles were rinsed with the Dam water before collection of samples, samples were filtered at point of collection, acidified with 1.5 mL concentrated HNO_3 for preservation, and then transported to the laboratory, at the laboratory; the samples were stored in refrigerator prior to analyses. The pretreated water samples were digested according to standard method as described by American Public Health Association (APHA, 1999).

Sediment samples were collected at same locations where water samples were obtained; the sediment samples were collected from top layer 3 – 10 cm of the riverbed and stored in clean airtight polythene bags. The sediment samples were treated with nitric acid to prevent the growth of microbes. The individual sediment samples were air dried at room temperature and ground with clean ceramic Teflon pestle and mortar, sieved, and reserved for wet digestion. The ground sediment samples were also digested according to standard method as described by American Public Health Association (APHA, 1999).

Metal Analysis

Heavy metal contents of the digests were determined using Microwave Plasma Atomic Emission Spectrophotometer (MPAES, model 4200, USA) in the Multi-User Science Research Laboratory of Chemistry Department, Ahmadu Bello University, Zaria. Calibration curves were prepared separately for each of the metals by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks. Average values of three replicates were taken for each determination and were subjected to statistical analysis. The metals determined include arsenic (As), chromium (Cr), lead (Pb), cadmium (Cd), and zinc (Zn). To evaluate the extent of heavy metal pollution, the results obtained from the analyses were subjected to different heavy metal indices analysis. The metal index methods applied were heavy metal pollution index (HPI) and the metal index (MI) (Tamasi and Cini, 2004; Kabir, *et al*., 2020) for evaluation of pollution level for water; while geo-accumulation index (*I*geo) was applied for the sediment pollution level (Jena, *et al*., 2019). The results obtained were also subjected to correlation analysis to assess levels of relationship.

HPI was calculated based on the Mohan, *et al*. (1996) model as given by Equation 1:

$$HPI = \frac{\sum_{i=0}^{n} W\acute{\imath}Q\acute{\imath}}{\sum_{i=0}^{n} W\acute{\imath}} \ldots\ldots Equation\ 1$$

Where: Wí = the reciprocal of the permissible limit (Si) of the íth heavy metal in water

The sub-index (Qí) of the parameter is calculated as expressed in Equation 2 :

$$Q\acute{\imath} = \sum_{n=1}^{n} \frac{|M\acute{\imath} - I\acute{\imath}|}{S\acute{\imath} - I\acute{\imath}}\ x\ 100 \ldots.\ Eqution\ 2$$

Where: Mi = monitored value of metal; Ií = standard (ideal) value of the íth metal (lowest acceptable limit); (Sí) = permissible limit (highest acceptable limit) of the íth heavy metal in water.

Metal Index (MI) for the water was calculated using the Tamasi and Cini (2004) model as presented by Equation 3:

$$MI = \sum_{\acute{\imath}=1}^{n} \frac{C\acute{\imath}}{MAC\acute{\imath}} \ldots\ldots Eqution\ 3$$

Where: Cí = measured concentrations of the íth heavy metal in the sample analyzed;
MACí = maximum allowed concentration (permissible limit) of the íth heavy metal.

Categorization/Classification of the HPI and MI values are given in Tables 1 and 2, World Health Organization (WHO) standards for heavy metals in drinking water (Table 4) were used for the HPI and MI calculations.

Table1: Metal Pollution Index (HPI) Classification.

Value Range	Characteristics
HPI< 100	Not polluted
HPI= 100	Threshold value
HPI> 100	Critically polluted

Kabir, et al. (2020)

Table 2: Metal Index (MI) Categorization/Classification.

Index Class	MI value Range	Characteristics
I	< 0.3	Very pure
II	0.3 – 1	Pure
III	1 – 2	Slightly polluted
IV	2 – 4	Moderately polluted
V	4 – 6	Strongly polluted
VI	> 6	Seriously polluted

Caerio, et al. (2005)

Table 3: Geo-Accumulation Index (Igeo) Classification.

Index Class	Igeo value Range	Characteristics
0	*I*geo < 0	Practically unpolluted
1	0 < *I*geo < 1	Unpolluted to moderately polluted
2	1 < *I*geo < 2	Moderately polluted
3	2 < *I*geo < 3	Moderately to heavily polluted
4	3 < *I*geo < 4	Heavily (strongly) polluted
5	4 < *I*geo < 5	Heavily to extremely polluted
6	*I*geo ≥ 5	Extremely polluted

Ogbeibu, et al. (2014) and Singh, et al. (2017)

The geo-accumulation index (Igeo) values for each metal were calculated using the Mullers's model of 1969 (Singh *et al*., 2017; Jena *et al*., 2019) as presented by Equation 4:

$$Igeo = log_2 \frac{\text{Cn}}{1.5\text{Bn}} \ldots\ldots\ldots\ldots. Equation\ 4$$

Where: Cn = measured concentration of element n in the sediments sample; Bn = geochemical background concentration for the element n; 1.5 is the factor compensating the background data (correction factor) due to lithogenic effects (Singh *et al*., 2017).

For Igeo computations, the average shale values (ASV) given by Turekian and Wedepohl (1961) as reported in Singh, *et al*. (2017) of As (13 mg/kg), Cr (90 mg/kg), Pb (20 mg/kg), Cd (0.3 mg/kg), and Zn (95 mg/kg) were used as the geochemical background concentration of the metals (Table 5). Categorization/Classification of Igeo values are given in Table 3.

RESULTS AND DISCUSSION

Heavy metals concentration levels in water and in sediment of River Kubani Dam are presented in Figures 2 and 3. Standard values are presented in Tables 4 and 5. From the results (Figure 2), Pb and Zn was not detected in the water sample from Site 3 and Site 4, respectively, but were detected alongside As, Cr and Cd in all sediment samples across Sites (Figure 3).

Figure 2: Heavy Metal concentrations in water

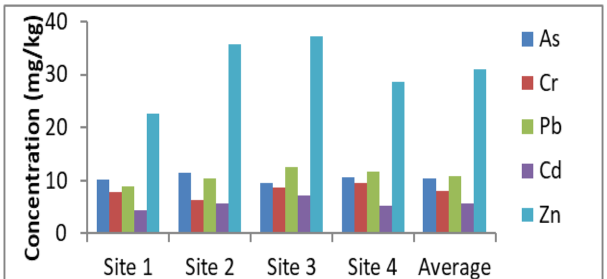

Figure 3: Heavy metal concentrations in sediment

The range of concentrations observed for metals in the water was 0.890 – 1.620 mg/L, 0.07 – 0.090 mg/L, 1.320 – 1.890 mg/L, 0.078 – 0.098 mg/L and 1.530 – 2.790 mg/L for As, Cr, Pb, Cd, and Zn, respectively. In the sediment, the range of concentration was 9.540 – 11.540 mg/kg, 6.340 – 9.450 mg/kg, 8.789 – 12.430 mg/kg, 4.430 – 7.230 mg/kg and 22.600 – 37.230 mg/kg for As, Cr, Pb, Cd and Zn respectively (Figure 3).

Table 4: Comparative Analysis of Heavy Metal Concentration of River Kubani Dam Water with World Health Organization (WHO) Standards and Permissible Limits.

Heavy Metals	Present study range (mg/L)	Average	[x] WHO standards	[y] WHO permissible limit
As	0.890 – 1.620	1.210	0.01	0.05
Cr	0.070 – 0.090	0.083	0.05	0.05
Pb	1.320 – 1.890	1.647	0.01	0.05
Cd	0.078 – 0.098	0.084	0.003	0.005
Zn	1.530 – 2.790	2.020	3	5

[x, y] WHO standard guideline for drinking water, 3rd ed. 2008 and 4th ed. 2022

Table 5: Comparative Analysis of Heavy Metal Concentration of River Kubani Dam Sediment with United State Environmental Agency (USEPA) Standards, Average Shale Values (ASV), Toxicity Reference Values (TRV), Threshold Effect Level (TEL).

Heavy Metals	Present study range (mg/kg)	Average	[a] USEPA sediment standards	[b]ASV	[c] TRV	[d] TEL
As	9.540 – 11.540	10.470	-	13		5.9
Cr	6.340 – 9.450	8.0530	43.4	90	26	37.3
Pb	8.789 – 12.430	10.805	35.8	20	31	35
Cd	4.430 – 7.230	5.688	0.99	0.3	0.6	0.6
Zn	22.600 – 37.230	31.018	121	95	110	123

a and c USEPA (1999) (Singh, et al., 2017); b Turekian and Wedepohl (1961) (Singh, et al., 2017); d TEL (MacDonald, et al., 2000)

Hence, there was more concentration in sediment than in the water, because sediments in aquatic environment serve as pool that can retain and release metals to the water column (Butu and Ati, 2013). More concentration observed in sediment aligns with the report by Adakole and Abolude (2012), when pollution status of the River kubanni Dam through metal concentrations in sediment and water columns was studied. The concentration (mg/L) range for each of the metals in the water with the exception of Zn exceeded the WHO standard and permissible limit of 0.01 and 0.05 for As, 0.05 and 0.05 for Cr, 0.01 and 0.05 for Pb, 0.003 and 0.005 for Cd, 3.00 and 5.00 for Zn (Table 4).

This exceedance from stipulated standard could come from the fact that River Kubani receives agricultural runoff and municipal wastewaters (Uzairu, *et al*., 2009; Butu and Ati, 2013). Higher concentration of metals in the water compared to WHO standard is consistent with the result obtained by Adakole and Abolude (2012) and Garba, *et al*. (2014), where the range of concentrations measured exceeded the standard limit as presented in Table 4.

Adakole and Abolude (2012), obtained concentrations range of 0.83 – 1.60 mg/kg for Pb, 0.01 – 0.04 mg/kg for Cd and 0.73 – 1.05 mg/kg for Cr; while Garba, *et al*. (2014) obtained concentrations range of 0.05 – 1.77 mg/kg for Cd and 0.05 – 2.57 mg/kg for Pb when water quality of the Dam was studied. Average concentration observed for Cr (8.053 mg/kg), Pb (10.805 mg/kg), and zn (31.018 mg/kg) in the sediment (in this study) were below the United State Environmental Protection Agency (USEPA) sediment standard of 43.4 mg/kg, 35.8 mg/kg and 121 mg/kg for Cr, Pb and Zn, respectively (Table 5). Meanwhile, Cd average concentration (5.688 mg/kg) exceeded the USEPA standard of 0.99 mg/kg.

The range of concentration for Cr (6.340 – 9.450 mg/kg), Pb (8.789 – 12.430 mg/kg), and Zn (22.600 – 37.230 mg/kg) in the sediment were all below the average shale value (ASV), toxicity reference value (TRV), threshold effect level (TEL) as presented in Table 5. Nevertheless, the concentration range for As (9.540 – 11.540 mg/kg) was higher than the TEL value (5.9 mg/kg), and also, the concentration range for Cd (4.430 – 7.230 mg/kg) was higher than the ASV (0.3 mg/kg), TRV (0.6 mg/kg) and TEL (0.6 mg/kg) for Cd.

Table 6: Heavy Metal Pollution Index (HPI) values for River Kubani Dam Water.

Metals	Site 1	Site 2	Site 3	Site 4
As	232.51	309.38	211.38	169.10
Cr	13.84	13.84	12.30	10.76
Pb	251.73	330.51	1.92	361.26
Cd	2882.40	3651.04	3074.56	2882.40
Zn	0.06	0.05	0.01	0.12
Overall HPI values	3380.53	4304.81	3300.16	3423.64

Table 7: Metal Index (MI) values for River Kubani Dam Water.

Metal	Site 1 Ci/MACi	Site 2 Ci/MACi	Site 3 Ci/MACi	Site 4 Ci/MACi
As	24.40	32.40	22.2	17.80
Cr	1.80	1.80	1.60	1.40
Pb	26.40	34.60	0	37.80
Cd	15.60	19.60	16.60	15.60
Zn	0.31	0.35	0.56	0
$MI = \sum(Ci/MACi)$	68.51	88.75	40.96	72.60

Based on WHO standard for drinking water and USEPA standard for sediment in Tables 4 and 5, Cd in River Kubani Dam exceeded the 0.005 mg/L WHO permissible limit for water and 0.99 mg/kg USEPA standard limit for sediment. This has disclosed that Cd was the main factor for River Kubani Dam water quality deterioration from heavy metal contamination as it pollutes both water and sediment. The high level of Cd in both water and sediment could result from run-off containing industrial waste, and minerals such as sphalerite (Zinc ore) into the river (Nnaji, *et al*., 2007; Balaram and Sawant, 2022), it could also have emanated from agro-chemicals, deteriorated galvanized plumbing material and certain fertilizers that found their way into the river.

Averagely, the predominance in concentration (mg/L) of the metals in water followed the order- Zn (2.020) > Pb (1.646) > As (1.210) > Cd (0.084) > Cr (0.083) as presented in Table 4, and in sediment, the concentration (mg/kg) was observed to flow in the order- Zn (31.018) > Pb (10.805) > As (10.470) > Cr (8.053) > Cd (5.688) as revealed in Table 5. Hence, Zn exhibited highest concentration in both water and sediment, however, its concentrations at all Sites and average concentrations of 2.020 mg/L in water and 31.018 mg/kg in sediment were below the 3 mg/L and 121 mg/kg WHO standard for drinking water and USEPA standard for sediment, respectively.

Outstanding concentration observed for Zn could result from Zn been released during weathering process and drained into the river. Zn high concentration in the river dam can also be attributed to loading of debris, household waste and fertilizers containing Zn into the dam from immediate communities (Butu and Ati, 2013).

The range of overall values (3300.16 – 4304.81) of HPI in Table 6, indicates that the Dam water was critically polluted at all Sites with respect to the heavy metals analyzed (Table 1), whereas Cr and Zn having individual HPI value range of 10.76 – 13.84 and 0.01 – 0.06, respectively, contributed less to the overall pollution level of the river. This is because the HPI values for Zn and Cr were far less than 100 (Table1), which is the threshold value for evaluation of pollution status using HPI (Kabir, *et al*., 2020). Cd contributed more to the overall pollution level of the river Dam as it exhibited highest range of HPI values (2882.40 – 3651.04).

The overall MI values of 68.51, 88.75, 40.96 and 72.60 for Sites 1, 2, 3, and 4, respectively, as shown in Table 7, also revealed that the overall quality of the river was not safe for drinking since the values fall under class VI of MI classification that signifies serious pollution of water bodies with respect to heavy metals.

Table 8: Geo-Accumulation Index (Igeo) Values for River Kubani Dam Sediment Analyses.

Sites	As	Cr	Pb	Cd	Zn
Site 1	-0.93	-4.12	-1.77	3.30	-2.66
Site 2	-0.76	-4.41	-1.54	3.68	-2.00
Site 3	-1.03	-3.96	-1.27	4.01	-1.94
Site 4	-0.88	-3.84	-1.36	3.57	-2.32
Range Min Max	-0.76 -0.93	-3.84 -4.41	-1.27 -1.77	3.30 4.01	-1.94 -2.66
Igeo value range	< 0	< 0	< 0	3.30 < *I*geo < 5	< 0
Igeo class	0	0	0	5	0

This implies that long time drinking of River Kubani Dam water may result to health hazards attributed to these metals. Pollution of the river Dam water by heavy metal observed in this study is consistent with the earlier findings of Adakole and Abulude. (2012) and Garba, *et al*. (2014) where the river Dam was reported to have been polluted by heavy metals including Chromium (Cr), Cadmium (Cd), lead (Pb), and mercury (Hg).

For River Kubani Dam sediment pollution status, geo-accumulation index (Igeo) revealed that the majority of the studied metals (As, Cr, Pb and Zn) have index value below zero (Igeo < 0), but Cd had Igeo value between 3.30 and 4.01 (Table 8), and falls within class 4 and 5 across Sites (Table 3). This indicates that the river Dam sediment was not polluted by As, Cr, Pb and Zn at all Sites, however, the river Dam sediment was heavily to extremely polluted by Cd especially at Site 3 with highest Igeo value of 4.01. This contrasts with the result obtained by Ekwuribe (2016), when heavy metal pollution status of the River Kubani Dam sediment was studied and where the sediment was not polluted by any of the metals studied including Cd. This could emanate from time difference between this study and that of Ekwuribe (2016) as Cd have accumulated over time.

From Table 9, the correlation analysis between metal concentrations in the sediment and in the water showed that As, Cd and Zn correlated positively with coefficient of correlation (r) at 0.65, 0.27, and 0.53, respectively. The concentrations of Cr and Pd in sediment showed negative correlation with their concentrations in water at r = - 0.089 (for Cr) and -0.45 (for Pb). The positive relationship between the levels of As, Cd and Zn in water and in sediment evidence that their sources were the same, while reverse could be said for Cr and Pd.

Table 9: Correlation between Metals Analyzed in Sediment and that in Water (p = 0.05).

Metals	Correlation Coefficient
As	0.65
Cr	- 0.89
Pb	- 0.45
Cd	0.27
Zn	0.53

CONCLUSION

The study aimed at evaluating the level of heavy metals (As, Cr, Pb, Cd, and Zn) pollution in water and sediment of River Kubanni Dam. Study revealed high concentration of these metals in the sediment compared to water. Correlation between metal concentrations in the sediment and in the water showed that As, Cd and Zn correlated positively, while that of Cr and Pb was negative.

Concentration of As, Cr, Pb, and Cd in the water were higher than the World Health Organization (WHO) Permissible limit. In the sediment, only Cd concentration was above the United State Environmental Protection Agency (USEPA), average shale value (ASV), toxicity reference value (TRV) and threshold effect level (TEL). Heavy metal pollution index (HPI) and metal index (MI) values show that the river water was critically and seriously polluted with the heavy metals, and Cd exhibited highest impact.

Geo-accumulation index (Igeo) values adjudged that the river sediment was not polluted by As, Cr, Pb, and Zn, however, the sediment was heavily to extremely polluted by Cd across Sites. Control of waste dumping and discharge of wastewater in the river is required to prevent the river from further heavy metal pollution.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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SUGGESTED CITATION

Okon, I.E., I.B. Anweting, and N.A. Nwokem. 2022. "A Study on Heavy Metals Pollution Levels in Water and Sediment of River Kubani Dam, Zaria, Nigeria". *Pacific Journal of Science and Technology*. 23(2): 107-116.

Pacific Journal of Science and Technology