Original Article

Radiological assessment and geochemical characterization of the sediments of Awba Dam, University of Ibadan, Nigeria

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Abstract

The distribution of natural radionuclides and geochemical parameters in the sediments of Awba Dam, University of Ibadan, Nigeria has been determined. The mean absorbed dose rates obtained were 72.3 nGy/h (upstream), 53.9 nGy/h (middle stream) and 50.29 nGy/h (downstream) with the corresponding mean annual effective dose rates of 0.09, 0.07 and 0.06 mSv/year, respectively. The geochemical analysis showed that Si, Al, Fe, Mn, Mg, Ca, Na, K, and Ti were the major elements and Zn, Cu, Cr, Rb, Ni, Ba, Ga, Ce, and Sr as heavy metals in the sediments. The moderate enrichment elements were Zn, Rb, Ba and Ga, whereas elements deficient in enrichment were Cr, Sr, Ce, Cu, and Ni. The geo-accumulation index was from unpolluted to moderately polluted environment. The enrichment factors (EF) observed in the elements indicate that these metals are entirely from crustal material or natural origin while EF >1.5 observed in Zn, Rb, Ba, and Ga suggests that the sources are more likely to be anthropogenic. The values of the radiological hazard parameter indices were below the recommended safe limits; an indication that the sediments can be used safely.

Keywords: Awba Dam, enrichment factor, geo-accumulation index, heavy metals, natural radionuclides, pollution, University of Ibadan

INTRODUCTION

The aquatic environments consist of an aqueous phase and a solid phase which is mainly sediment (particulates) in surface environments and the host bedrock in groundwater.[1] Since sediment is an integral part of an aquatic ecosystem, naturally occurring primordial radionuclides are found to trap in the sediment. Concerted attention should be given to the distribution pattern of naturally occurring radionuclides and thorough study of environmental materials that serve as reservoir of the natural radioactivity. Due to weathering and other environmental processes, radionuclides in rock and soil may accumulate in sediment and dissolve into drinking water, thereby leading to human exposure.[2] The earth crust also contains small amount of ^{238}U, ^{232}Th, ^{40}K and other heavy and major elements such as Cs, Cd, Pb, Fe, Mg, Mn, Cu, Zn, Cr, As, and Ni. The concentrations of all these elements depend on the geology of a local environment as well as other natural and anthropogenic processes.[3] Pollution of natural environment by metals has been a major problem because these metals are non-destructible and many of them have toxic effects on living organisms, especially when they exceed certain threshold of safety limits.[4]

Sediment forms a major component of an ecosystem and is the most endangered due to the influence of

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various human activities. Sediment is considered contaminated when chemicals are present or other alterations have been made to its natural environment.[5] Considering this fact, radioactivity in a water body can remain at significant levels as a result of secondary contamination processes. Due to gravitational and other depositional phenomena, the highest proportion of the radioactive materials is mainly found in the sediment compartment of the aquatic ecosystem.[6] Thus, river sediment is considered a durable and reliable register of the river pollution by radionuclides.[7] Studies on natural radioactivity and heavy metals are necessary, not only because of their radiological and pollutant impacts to human health, but they also serve as excellent biochemical and geochemical tracers in the environment and environmental monitoring.[8]

The Awba Dam, since 1964 provides water for the domestic needs of the university, opportunities for fish culture and to facilitate fisheries research and also serves as source of revenue. There has not been effective and regular control of environmental and human waste entering the dam and this has been a concern to many due to danger that may arise from these pollutants. No study on radionuclide and heavy metal distributions has been carried out on the Awba Dam of the University of Ibadan, Nigeria despite the level of discharges into the dam, from laboratories, runoffs from farms and discharges from national institute for radiation protection and research. This study is, therefore, aimed to determine the level of natural radionuclides and heavy metals distribution in the sediments of the dam with a view to characterizing the geochemical parameters and the radiological implications to the population of the University of Ibadan community.

MATERIALS AND METHODS

Description of sampling location

The Awba Reservoir in the university lies between the latitudes 7°26′–7°27′N and longitudes 3°53′–3°54′E located in the South Western region of Nigeria about 160 km from the Atlantic Ocean coast at an altitude of 185 m above sea level. With a maximum depth of 5.5, 140 m long with a crest of 12.2 m, the reservoir can hold about 230 million liters of water. The stream throughout its course in the university has a length of 975 m.[9] The dam is of enormous importance to the University of Ibadan community as a source of water, fish, and sand for building, recreation, and tourism purposes.

Collection of samples

A total of 31 sediment samples were collected across the dam. The samples were collected at a depth of 0–15 cm from the upstream, the downstream and the middle locations of the dam. The map of University of Ibadan showing the dam and the locations from where samples were collected is shown in Figure 1. After collection, the samples were placed in polythene bags and carefully labeled to prevent sample contamination. The samples were analyzed for their natural radioactivity content at Radiation and Health Physics Research Laboratory at the Department of Physics, University of Ibadan, while geochemical analyses were performed at geology department of the university.

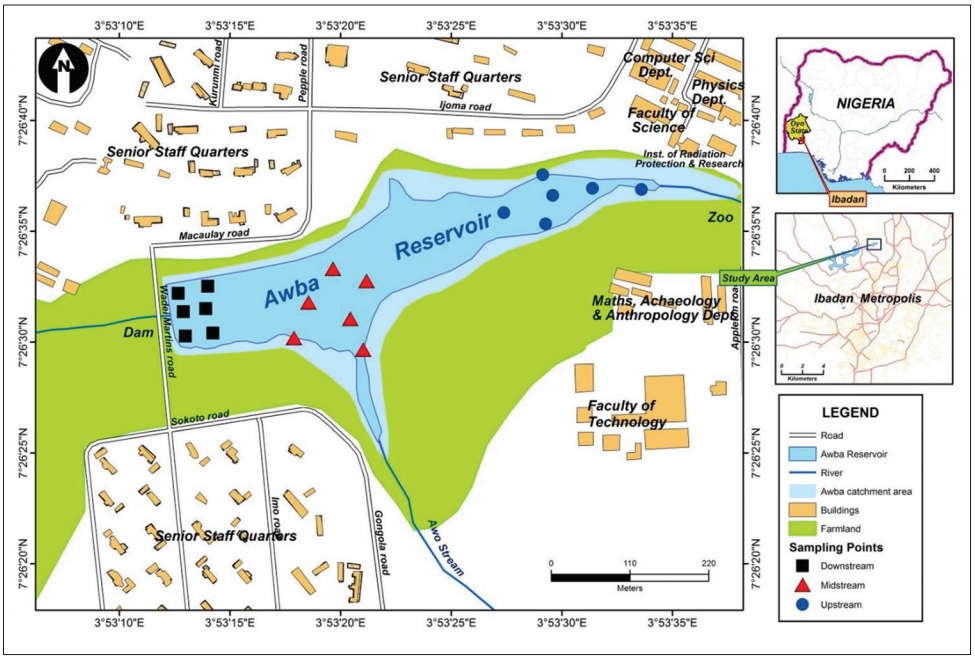

Figure 1: The map of the University of Ibadan campus showing the Awba Dam and sampling points

Samples preparation for radionuclides determination

The samples were air-dried, homogenized, crushed, and sieved to pass through a 2 mm mesh. The samples were further oven-dried to remove moisture at 110°C until a constant weight was reached. Thereafter, approximately 200 g of each of the samples was transferred to a cleaned, washed and uncontaminated cylindrical plastic container of size 8.5 cm length, and 7.5 cm diameter and sealed. The sealed samples were counted after a minimum period of 28 days to achieve secular equilibrium between ^{226}Ra and its short-lived progenies.

Sample preparation for geochemical parameters

Twenty representative samples out of the 31 samples used for the radionuclides analysis were used in the elemental analysis. Each sample was first pulverized and 0.5 g digested with 5 ml HF and a mixture of prepared solution of nitric acid and perchloric acid (ratio 3:2) according to USEPA method 3052.[10] The sample was stirred and heated inside a fume cupboard. The digested sample was diluted with distilled water and made up to 20 ml mark. A volume of 1 ml was taken from the solution and further diluted with distilled water to 10 ml mark. The major elements Si, Al, Fe, Mn, Mg, Ca, Na, K, and Ti were then determined using a Perkin Elmer 305 Atomic Absorption Spectrophotometer. Similarly, the heavy metals Zn, Cu, Cr, Rb, Ni, Ba, Ga, Ce, and Sr were also determined.

Activity concentration determination

The radioactivity counting was done using an ORTEC Coaxial n-type high purity germanium detector with 20% relative efficiency coupled to ORTEC multichannel analyzer. The detector is placed inside a cylindrical lead shield of 5 cm thickness with internal diameter of 24 cm and height of 60 cm. The lead shield is lined with various layers of copper, cadmium and Plexiglas each of 3 mm thick. The efficiency of the detector system was determined using standard reference, IAEA sediment sample (IAEA-315) containing ^{40}K, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{228}Th, ^{232}Th, ^{234}U, and ^{238}U. The standard reference sample and sediment samples having identical size, shape, density, spatial distribution of material, etc., were counted for 10 h under similar condition. The activity concentration of each radionuclide in the samples was obtained using the Equation 1:[11]

$$A_{E_i} = \frac{N_{E_i}}{\varepsilon_{E_i} \times T \times \gamma_{E_i} \times M} \quad (1)$$

Where A_{E_i} is the activity concentration of measured samples, N_{E_i} is the net peak area at energy E of radionuclides, ε_{E_i} is the detector efficiency, T is the counting time (10 h), γ_{E_i} is the number of gamma per nuclear transformation, and M is the mass in kilograms of the measured sample and ε_{E_i} is the detector efficiency which is given by:

$$\varepsilon_{E_i} = \frac{C_n}{T \times \gamma_{E_i} \times M \times C} \quad (2)$$

Where C_n is the net area of the standard sample, C is the activity of the standard sample in Bq/kg, T, γ_{E_i} and ε_{E_i} assumed the same value as given in Equation 1. The gamma lines 186.211 keV of ^{226}Ra, 609.316, 1120.287 and 1764.539 keV of ^{214}Bi were used to determine ^{226}Ra (^{238}U) while the gamma lines 911 keV of ^{228}Ac, 583.187 and 2614.511 keV of ^{208}Tl were used to determine ^{232}Th and that of ^{40}K was determined from the gamma line of 1460.822 keV. Using Equation 1, the activity concentrations of the radionuclides is presented in Table 1.

The minimum detectable activity (MDA) for ^{40}K, ^{226}Ra and ^{232}Th in the sediment were determined using Equation 3:

$$\text{MDA} = \frac{\text{LLD}}{\varepsilon \times \gamma \times m \times t} \quad (3)$$

Where, $\text{LLD} = 4.653 \times \sqrt{\text{Background count}}$

Where LLD is lower limit of detection and ε, β, m, and t assumed the same value as given in Equation 1. The values of the MDA of the detector for ^{40}K, ^{226}Ra, and ^{232}Th are 23.4, 12.0 and 16.4 Bq/kg, respectively.

Absorbed dose rate

The absorbed dose rate at 1 m above the ground (nGy/h) was calculated using the expression given by UNSCEAR 2000:[12]

$$\text{DR}\,(\text{nGy/h}) = 0.462A_{\text{Ra}} + 0.604A_{\text{Th}} + 0.0417A_{\text{K}} \quad (4)$$

Where DR is the absorbed dose rate in nGy/h and A_{Ra}, A_{Th} and A_{K} are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K, respectively. The annual effective dose (AED) to the public due to the absorbed dose rate in air was calculated in unit of mSv/year by converting the total absorbed dose in nGy/h using 0.7 Sv/Gy as conversion factor (CF) and multiplying by occupancy factor (OF) using Equation 5:

$$\text{AED} = \text{DR}_i \times 0.2 \times 24 \times 365 \times 0.7 \quad (5)$$

Where, 0.7 Sv/Gy is the CF[13] for absorbed dose in air to external effective dose, and 0.2 represents the outdoor OF. This shows that the people in the study area spend approximately 20% of their time outdoors. The result of the absorbed dose rate and the AED rate are presented in Table 1.

Table 1: Activity concentrations (Bq/kg), absorbed dose and annual effective dose of primordial radionuclides in up, middle and down streams locations of the dam

Sample code	^{40}K	^{232}Th	^{226}Ra	Absorbed dose (nGy/h)	Annual effective dose rate (mSv/year)
UP01	250.9±19.2	59.6±8.2	44.0±13.1	66.8	0.08
UP03	285.0±21.2	67.2±9.2	53.6±16.0	77.2	0.09
UP04	285.0±21.2	61.2±8.3	53.1±16.1	73.4	0.09
UP05	243.2±18.5	67.3±9.3	52.7±16.4	75.1	0.09
UP06	284.6±21.4	69.6±9.5	54.8±16.5	79.2	0.10
UP07	278.6±20.8	61.7±8.6	48.0±14.0	71.1	0.09
UP08	262.9±20.0	68.7±9.4	51.5±15.6	76.3	0.09
UP09	266.9±19.9	68.8±9.4	53.3±16.3	77.3	0.09
UP10	240.0±18.2	45.7±6.4	35.6±10.5	54.1	0.07
MD01	75.3±7.3	51.7±7.2	38.2±11.4	52.0	0.06
MD02	249.4±18.6	67.0±9.1	42.6±12.8	70.5	0.09
MD03	60.1±6.7	47.8±6.7	33.3±9.9	46.8	0.06
MD04	154.9±12.5	61.7±8.4	44.3±13.4	64.2	0.08
MD05	78.7±7.9	41.1±5.7	31.9±9.6	42.8	0.05
MD06	111.4±10.4	67.2±9.3	52.8±16.0	69.6	0.09
MD07	80.7±8.1	50.3±7.0	34.6±11.1	49.7	0.06
MD08	66.3±7.4	40.1±5.6	28.2±8.6	40.0	0.05
MD09	86.0±7.9	50.0±6.9	31.5±9.3	48.4	0.06
MD10	103.2±9.4	47.4±6.6	40.2±12.4	51.5	0.06
MD11	152.7±12.7	53.1±7.2	42.3±13.1	58.0	0.07
DW01	87.5±9.1	52.9±7.4	40.3±12.5	54.2	0.07
DW02	115.8±9.8	42.5±6.1	30.2±9.1	44.4	0.05
DW03	113.1±10.1	43.4±6.0	30.9±9.5	45.2	0.06
DW04	73.2±8.5	50.0±6.9	35.0±11.2	49.4	0.06
DW05	73.7±7.1	38.3±5.4	26.2±8.2	38.3	0.05
DW06	85.9±8.2	47.4±6.6	33.6±10.8	47.7	0.06
DW07	82.2±7.9	46.8±6.4	32.6±10.3	46.7	0.06
DW08	115.3±10.4	56.9±7.9	40.6±12.8	57.9	0.07
DW09	147.3±12.3	59.8±8.2	45.9±14.2	63.5	0.08
DW10	129.3±11.1	51.9±7.2	33.9±10.0	52.4	0.06
DW12	113.1±10.0	49.5±6.8	38.2±11.7	52.3	0.06

Radiation hazard indices

Radium equivalent activity

Radium equivalent is a common radiological index in comparing the specific activities of sediment samples containing ^{226}Ra, ^{232}Th, and ^{40}K by a single quantity, which takes into account the radiation hazards associated with them.[14] The radium equivalent activity (Ra_{eq}) is mathematically defined as below.[15]

$$Ra_{eq}\ (Bq/kg) = C_{Ra} + 1.43C_{Th} + 0.077C_{K} \quad (6)$$

The value of Ra_{eq} must be <370 Bq/kg for the radiation hazard to be negligible. The results obtained are presented in Table 2.

Internal radiation hazard index

The internal radiation hazard index (H_{in}) is used to reduce the maximum permissible concentration of ^{226}Ra to half the values appropriate for the external exposure alone.[16] The inhalation of gaseous radionuclide, radon-222 which is the daughter product of ^{226}Ra might result in obtaining internal exposure. The internal exposure to ^{222}Rn and its radioactive progeny can be estimated in terms of H_{in} as below.

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_{K}}{4810} \quad (7)$$

The results obtained are presented in Table 2.

External radiation hazard index

The external hazard index (H_{ex}) due to gamma radiation is calculated using Equation 8.[17]

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_{K}}{4810} \quad (8)$$

To limit the external gamma dose of materials to 1.5 mGy/year for the radiation hazard to be negligible or insignificant, the H_{ex} must be in conformity with the

Table 2: Radium equivalent, internal, external hazard index and gamma representative index for upstream, middle and downstream in the sediments of Awba Dam

Serial number	Sample code	Ra_{eq} (Bq/kg)	H_{in}	H_{ex}	$I_{\gamma r}$
1	UP01	148.5	0.52	0.40	1.06
2	UP03	171.7	0.61	0.46	1.22
3	UP04	162.6	0.58	0.44	1.16
4	UP05	167.6	0.59	0.45	1.19
5	UP06	176.3	0.62	0.48	1.25
6	UP07	157.7	0.56	0.43	1.12
7	UP08	170.0	0.60	0.46	1.21
8	UP09	172.3	0.61	0.47	1.22
9	UP10	119.5	0.42	0.32	0.85
10	MD01	117.9	0.42	0.32	0.82
11	MD02	157.6	0.54	0.43	1.12
12	MD03	106.4	0.38	0.29	0.74
13	MD04	144.5	0.51	0.39	1.02
14	MD05	96.7	0.35	0.26	0.68
15	MD06	157.4	0.57	0.43	1.10
16	MD07	112.7	0.40	0.30	0.79
17	MD08	90.5	0.32	0.24	0.63
18	MD09	109.7	0.38	0.30	0.77
19	MD10	116.0	0.42	0.31	0.81
20	MD11	130.1	0.47	0.35	0.92
21	DW01	122.7	0.44	0.33	0.86
22	DW02	99.9	0.35	0.27	0.70
23	DW03	101.7	0.36	0.27	0.72
24	DW04	112.1	0.40	0.30	0.78
25	DW05	86.7	0.30	0.23	0.61
26	DW06	107.9	0.38	0.29	0.75
27	DW07	105.8	0.37	0.29	0.74
28	DW08	130.8	0.46	0.35	0.92
29	DW09	142.8	0.51	0.39	1.00
30	DW10	118.1	0.41	0.32	0.83
31	DW12	117.7	0.42	0.32	0.83
Mean±SD		130.1±26.9	0.46±0.10	0.35±0.07	0.92±0.19

SD: Standard deviation, Ra_{eq}: Radium equivalent activity, H_{in}: Internal hazard index, H_{ex}: External hazard index, $I_{\gamma r}$: Representative gamma index

criterion of $H_{ex} \leq 1$.[18] The results obtained are presented in Table 2.

Representative gamma index

The representative gamma index ($I_{\gamma r}$) used to estimate the level of γ - radiation hazard associated with the natural radionuclides in specific investigated samples was determined using the expression proposed by NEA-OECD[19] and given by Equation 9.

$$I_{\gamma r} = \frac{C_{Ra}}{150} + \frac{C_{Th}}{100} + \frac{C_K}{1500} \quad (9)$$

The results obtained are presented in Table 2.

RESULTS AND DISCUSSION

Activity concentrations of the radionuclides in the sediment

The activity concentrations of ^{40}K, ^{232}Th, and ^{226}Ra in the sediments samples are presented in Table 1. The average concentration of ^{40}K, ^{232}Th, and ^{226}Ra in the upstream are 266.4 ± 20.0, 63.3 ± 8.7 and 49.6 ± 14.9 Bq/kg, respectively. The concentration of ^{40}K, ^{232}Th and ^{226}Ra in Bq/kg at the middle stream are 110.8 ± 9.9, 52.5 ± 7.3, and 38.2 ± 11.6, respectively. Similarly, the same pattern was observed at downstream of the dam, the average concentration of ^{40}K, ^{232}Th, and ^{226}Ra are 103.3 ± 9.5, 49.0 ± 6.8 and 35.2 ± 10.9 Bq/kg, respectively.

The pattern of distribution observed in the radionuclides at the upstream of the dam may be due to the fact that more pollutants are channeled into the dam from this end such as effluents from domestic, industrial, and laboratory waste from students' hostels, National Institute for Radiation Protection and Research and Faculty of Science Demonstration Laboratories. Furthermore, the waste products from aquarium and runoffs of fertilizer from nearby farms find their way to the dam. However, the activity concentrations obtained in this study were in agreement with other research works[16,20,21] conducted on sediments in different part of Southwest Nigeria. Furthermore, in comparison with results obtained from other parts of the world, we can infer from Table 3 that ^{40}K activity is much lower whereas ^{232}Th and ^{226}Ra activity levels are comparatively higher. The range of values of ^{40}K and ^{226}Ra observed in this study are within the range of values for crustal concentrations of 140–820 Bq/kg for ^{40}K, 11–64 Bq/kg for ^{232}Th (exception for ^{232}Th which is slightly high) and 16–110 Bq/kg for ^{238}U (^{226}Ra) as reported in UNSCEAR 2000[12] for area with high background radiation levels around the world. From Table 3, the mean activity concentrations of the radionuclides decrease in the order $^{40}K > ^{232}Th > ^{226}Ra$. The higher radioactive levels of ^{40}K seen in the study area may be associated with the granite rocks which break down as a result of weathering and transport to the dam to form sediment [Figures 2 and 3].

Dose assessment

As could be observed from Table 1 the absorbed dose rates obtained ranged from 54.1 to 79.2 nGy/h, 40.0 to 70.5 nGy/h, and 38.3 to 63.5 nGy/h for upstream, middle, and downstream respectively, whereas the mean was 72.3 nGy/h for upstream, 54.0 nGy/h for middle stream, and 50.2 nGy/h for downstream. The AED rate ranged from 0.07 to 0.10 mSv/year for upstream, 0.05 to 0.09 mSv/year for middle stream, and 0.05 to 0.08 mSv/year for downstream. The average value of 0.07 mSv/year obtained from the study

Table 3: Activity concentrations of naturally occurring radionuclides obtained by different authors in other parts of the world

Country	Lake/river	^{40}K	^{232}Th	^{226}Ra	Reference
Bangladesh	Shango river	255	25.4	57.5	[22]
	Karnapulli river	272	37.9	65.5	[22]
China	Wei river	833.3	21.8	33.1	[23]
	Nile river	200.21	16.30	12.94	[24]
	Lake nasser	317.6	14.3	18.4	[25]
India	Kali river	394.7	40.1	6.9	[26]
	Sharavathi river	493.4	72.0	11.6	[27]
	Palar river	472.0	10.0	36.0	[28]
Pakistan	Hunza river	173.96	21.37	11.65	[29]
Turkey	Coruh river	510.2	18.3	11.4	[30]
	Altunkaya lake	460.0	19.5	27.7	[31]
Nigeria	Ogun river	499.48	12.65	11.78	[32]
	Twenty lakes	549.3	62.0	27.9	[31]
	Osun river	182.05	13.85	20.75	[21]
	Awba Dam	153.3±12.7	54.4±7.5	40.5±12.3	Present study

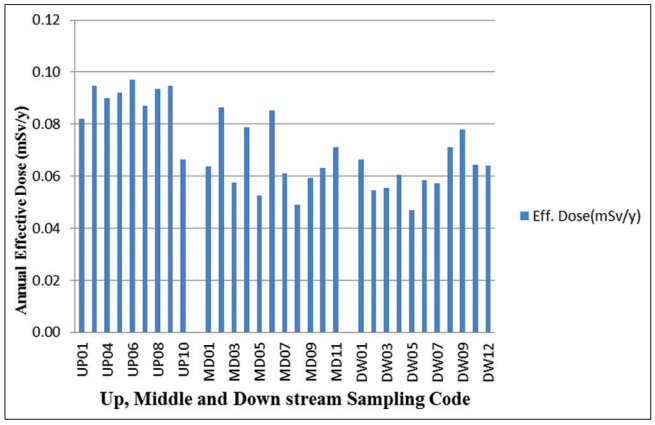

Figure 2: The annual effective dose in the upstream, middle and down streams location

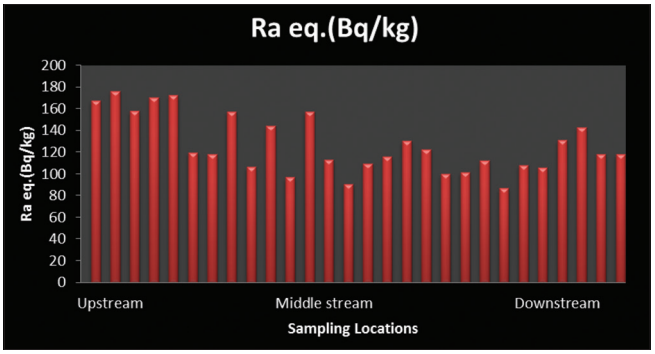

Figure 3: The radium equivalent for up, middle and down streams

compared well with recommended annual outdoor dose limit for members of the public far from nuclear facilities by the UNSCEAR.[13]

Radiological assessment

Radium equivalent gives the useful guideline in the regulation of the safety standards on radiation protection for the general public.[10] As shown in Table 2, all the values (up, middle, and down streams) are within the recommended value of 370 Bq/kg. When these values were compared with the values obtained for Osun river,[21] it could be observed that the value for Osun river also decreased down the river having its highest value at the upper region and the least at the lower region. Both hazard indices, external and internal, are much below unity. These results suggest that radiation hazard associated with the sediment samples when used as building material would not pose any health effects. The sediment samples at the Upstream exceed the upper limit for $I_{\gamma r}$ which is unity, whereas the sediment samples at the middle and down streams are below one. This suggests that at the upper stream of the dam, there are relatively higher concentrations of the natural radionuclides, albeit low, as may be seen Table 1 when compared with middle and lower streams of the dam.

Geochemical assessment

The concentrations of the trace elements in the sediment samples from the selected sampling points are presented in Table 4. The highest mean concentration of the trace elements was Ba while the lowest was Ce. The order of increased magnitude was Ce < Ga < Cu < Ni < Rb < Sr < Cr < Zn < Ba. From Table 4, it is observed that the concentration of Cu was between 20.38 and 39.56 ppm while that of Pb and Zn range from 12.60 to 23.14 ppm and 210.00 to 393.10 ppm, respectively. The high relative abundance of these elements may suggest possible replacement during and

after diagenesis. In general, Rb, Cu, and Ba were clearly associated with clay minerals.

The results of the analysis of the major elements are presented in Table 5. The result showed a slight variation in elemental composition of all the sample sets. This variation was due to different components constituting the sediment samples; reflecting the homogeneity of the sediment suite and indicating constancy of provenance and sedimentary environment of the material. The pattern observed in the sediments was SiO_2 > Al_2O_3 > Fe_2O_3 > MgO > CaO > TiO_2 > K_2O > Na_2O > MnO. Chemical composition is closely dependent on grain size, with Al_2O_3 increasing toward finer sediments and SiO_2 toward sands. This strongly has control on mineralogical composition, in which clay minerals dominate the fine fraction, and quartz the coarse fraction. The SiO_2 content is relatively high as shown in Table 5. Mineralogical studies have shown that SiO_2 is mainly present as quartz, both fine as well as coarse-grained. Cursory examinations have revealed the rare presence of diatoms and sponge spicules, suggesting that these are not important sources of Si in these sediments. The CaO content generally >1% indicates slight calcareous sediments. This is derived from skeletal components and therefore is biogenous. The distribution of Al_2O_3, TiO_2, and Fe_2O_3 helps in understanding the sources of elements and geochemical environment of sedimentation. Al is mainly held in the clay mineral lattices as an essential constituent. This is also evident from the similarity of the distribution pattern of Al_2O_3 with respect to textural distribution. The contribution of Al_2O_3 by resistant detrital minerals is considerably less than that of clay mineral contribution. The TiO_2 content of these sediments mainly comes from the detrital minerals as seen from its higher concentration (average 1.21%) in the sample sets. Corroborative investigations have shown the presence of large quantities of opaques in these sediments.

Distribution patterns of MgO, Na_2O, and K_2O and their correlations with Al_2O_3 [Table 5] indicate that clay minerals are important host minerals for these elements. In addition to their initial presence in crystal lattices of clay minerals, exchange for Ca and absorption processes cause fixation of Mg, Na, and K in river-borne clays when these are brought into contact with seawater.

Table 4: Concentrations of heavy metals in sediments of Awba Dam

Elements	Range (mean±SD)			Average crustal value (%)[33]
	Upstream	Middle stream	Down stream	
Number of samples	7	6	7	
Zn (ppm)	210.62-393.10 (288.12±67.55)	211.15-330.14 (259.70±44.62)	201.15-336.35 (263.15±57.50)	80
Cu (ppm)	20.62-39.10 (30.02±7.45)	20.38-39.56 (29.22±5.65)	20.38-39.56 (29.26±6.97)	75
Cr (ppm)	112.36-133.23 (123.96±9.53)	112.10-133.13 (117.53±7.54)	110.77-133.60 (125.01±8.75)	185
Rb (ppm)	21.32-56.96 (36.92±12.31)	17.20-312.54 (144.36±109.80)	42.60-223.14 (142.56±73.02)	32
Ni (ppm)	33.10-34.65 (34.08±0.50)	32.31-33.85 (31.56±3.71)	31.40-36.53 (33.05±1.56)	105
Ba (ppm)	555.48-932.48 (800.23±121.59)	672.67-992.52 (831.64±121.37)	535.48-972.36 (819.29±147.84)	250
Ga (ppm)	16.02-33.61 (25.68±8.16)	20.34-36.91 (27.21±5.23)	16.33-33.12 (27.54±5.55)	18
Ce (ppm)	15.65-30.34 (23.08±5.51)	11.78-29.67 (17.87±6.28)	2.78-19.22 (11.45±5.94)	33
Sr (ppm)	11.96-40.85 (21.82±12.18)	14.88-448.21 (226.40±137.62)	11.45-342.77 (113.53±129.18)	215

SD: Standard deviation

Table 5: Concentrations of major elements in sediments of Awba Dam

Elements	Range (mean±SD)			Average crustal value (%)[33]
	Upstream	Middle stream	Downstream	
Number of samples	7	6	7	
SiO_2 (%)	55.7-59.38 (56.96±1.39)	54.57-56.46 55.49±0.73	56.46-58.54 (57.22±0.78)	26.80
Al_2O_3 (%)	25.78-30.27 (28.56±1.56)	29.02-31.27 (30.14±0.71)	26.06-29.86 (28.42±1.16)	8.41
Fe_2O_3 (%)	4.06-10.39 (5.32±2.09)	4.66-5.08 (4.88±0.14)	3.52-5.05 (4.65±0.47)	
MnO (%)	0.06-0.08 (0.07±0.01)	0.06-0.08 (0.07±0.01)	0.06-0.07 (0.07±0.00)	1400 (ppm)
MgO (%)	4.10-5.08 (4.59±0.29)	4.29-4.97 (4.68±0.20)	4.13-4.65 (4.41±0.19)	3.2
CaO (%)	1.45-1.66 (1.57±0.06)	1.60-1.75 (1.66±0.05)	1.46-1.61 (1.54±0.04)	5.29
Na_2O (%)	0.73-0.9 (0.82±0.06)	0.83-0.91 (0.87±0.03)	0.76-0.83 (0.81±0.02)	2.3
K_2O (%)	0.78-1.01 (0.90±0.08)	0.83-1.11 (0.95±0.10)	0.80-0.98 (0.91±0.06)	0.91
TiO_2 (%)	1.02-1.23 (1.14±0.06)	1.13-1.25 (1.21±0.04)	1.07-1.21 (1.14±0.04)	0.54

SD: Standard deviation

Enrichment factor and geo-accumulation index

In the assessment of the degree of pollution of the dam sediments by heavy metals; there is need to evaluate the enrichment factor (EF) value. To distinguish the heavy metals originating from human activities from those originating from natural weathering, calculation of EF is an essential part of geochemical studies.[34] As proposed by Simex and Helz,[35] EF as employed to assess the degree of contamination and to understand the distribution of the elements of anthropogenic origin from sites by individual elements in sediments. Fe was chosen as the normalizing element while determining EF-values since in wetlands it is mainly supplied from sediments and is one of the widely used reference elements.

$$EF = \frac{C_n / C_{ref}}{B_n / B_{ref}} \quad (10)$$

Where, C_n is the concentration of element "n" in the sediment sample examined, C_{ref} is the concentration in the earth crust,[36] B_n denote the reference element and B_{ref} represents the concentration of the element in continental crust. The world average elemental concentrations reported by Turekian and Wedepohl 1961[33] in the earth's crust were used as a reference in this study because regional geochemical background values for these elements were not available. Five contamination categories are recognized on the basis of the EF as given by Sutherland.[37]

The result of the EF for heavy metals and major elements is presented in Table 6. The higher EF values are observed in the order of Zn > Rb > Ba > Ga > Cr > Sr > Ce > Cu > Ni for trace elements (heavy metals). Based on the classification given above the moderate enrichment elements are Zn, Rb, Ba, and Ga while elements that are deficient in enrichment are Cr, Sr, Ce, Cu, and Ni. The minimum EFs less than unity observed in these samples imply that these elements are depleted in some of the phases relative to crustal abundances in the study area. The EFs value observed in Cr, Sr, Ce, Cu, and Ni indicates that these metals are entirely from crustal material or natural origin while EF > 1.5 as observed in Zn, Rb, Ba, and Ga suggests that the sources are more likely to be anthropogenic.[38] Similar observation was made for the major elements as could be seen in Table 6. The higher values in order of Al_2O_3 > TiO_2 > SiO_2 > MgO with the exception of K_2O > Na_2O > CaO > MnO having EF <1.5 indicating crustal material or natural origin.

A common approach to estimating the enrichment of metal concentrations above background or baseline concentrations is to calculate the geo-accumulation index (I_{geo}) as proposed by Müller.[39] The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index. This index is calculated as follows: The classification is shown in Table 7[34]

$$I_{geo} = \log_2 \left\{ \frac{C_n}{1.5B_n} \right\} \quad (11)$$

Where C_n is the concentration of the element in the enriched samples, and B_n is the background or pristine value of the element. The factor 1.5 is introduced to minimize the effect of possible variations in the background values attributed to lithologic variations in the sediments. The result of the I_{geo} for both heavy metals and major elements is shown in Tables 6 and 8. The pollution level of the dam with heavy metals and major elements ranged from unpolluted to moderately polluted as shown in Tables 5 and 6.

The results of the Pearson correlation coefficients between the activity concentration and trace metals and major elements are presented in Tables 9 and 10. From Table 9 the analysis revealed that Ce had significant positive correlation with the primordial radionuclides while Sr and Rb had negative correlation with ^{238}U and ^{232}Th, respectively, and the remaining of the trace elements did not correlate with primordial radionuclides. This may suggest that they have similar source. Similarly, a significant correlation was observed between the activity

Table 6: The enrichment factor of heavy metals in the sediments

Heavy metals	Mean value (ppm)	Reference value (ppm)	EF	I_{geo}	I_{geo} class
Zn	270.86	80	4.82	1.17	Moderately polluted
Cu	29.51	75	0.56	−1.90	Unpolluted
Cr	122.40	185	0.94	−1.18	Unpolluted
Rb	106.12	32	4.72	1.14	Moderately polluted
Ni	32.96	105	0.45	−2.26	Unpolluted
Ba	816.32	250	4.65	1.12	Moderately polluted
Ga	26.79	18	2.12	−0.01	Unpolluted
Ce	17.45	33	0.75	−1.50	Unpolluted
Sr	115.29	215	0.76	−1.48	Unpolluted

EF: Enrichment factor, I_{geo}: Geo-accumulation index

concentration of the primordial radionuclides and some of the major elements. Na_2O correlated with all the three radionuclides at 0.01 and 0.05 level. Furthermore, TiO_2 had a significant correlation with ^{232}Th and ^{238}U while MgO correlated with ^{40}K and ^{232}Th.

CONCLUSIONS

The activity concentrations of naturally occurring radionuclides and geochemical parameters in sediments of Awba Dam have been determined. The mean AED due to sediments of the dam was well compared with recommended safe limit, and the radiological hazard indices were lower than the recommended international safe limits. The results obtained showed that the environment of Awba Dam is radiologically safe. This is an indication that the sediments of Awba Dam can be used for the construction of buildings without causing any radiation hazard. The I_{geo} showed that the degree of pollution in the dam was from unpolluted to the moderately polluted environment. The EFs for Cr, Sr, Ce, Cu, and Ni indicates that they are from crustal material while EF >1.5 for Zn, Rb, Ba and Ga suggests that the sources are more likely to be anthropogenic. These calculated parameters, however, could serve as baseline information for future reference and epidemiological studies of the dam.

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Conflicts of interest

There are no conflicts of interest.

Table 7: Classification table for geo-accumulation index

I_{geo}	I_{geo} class	Designation of sediment quality
≤0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly polluted to extremely polluted
≥5	6	Extremely polluted

I_{geo}: Geo-accumulation index. Source: Rezaee *et al*.

Table 8: Enrichment factor for major elements

Major elements	Mean value (%)	Standard reference value (%)	EF	I_{geo}	I_{geo} class
SiO_2	56.61	26.8	3.01	0.49	Unpolluted to moderately polluted
Al_2O_3	28.98	8.41	4.91	1.20	Moderately polluted
MnO	0.07	1400 (ppm)	0.07	−4.90	Unpolluted
MgO	4.56	3.20	2.03	−0.07	Unpolluted
CaO	1.59	5.29	0.43	−2.30	Unpolluted
Na_2O	0.83	2.30	0.51	−2.06	Unpolluted
K_2O	0.92	0.91	1.44	−0.57	Unpolluted
TiO_2	1.16	0.54	3.06	0.52	Unpolluted to moderately polluted

EF: Enrichment factor

Table 9: Pearson correlation matrix of activity concentrations and heavy metals of Awba Dam sediments

	^{40}K	^{232}Th	^{238}U	Zn	Cu	Cr	Rb	Ni	Ba	Ga	Ce	Sr
^{40}K	1											
^{232}Th	0.761**	1										
^{238}U	0.786**	0.939**	1									
Zn	0.218	−0.035	0.149	1								
Cu	0.169	0.189	0.097	0.237	1							
Cr	−0.192	−0.284	−0.216	0.311	−0.124	1						
Rb	−0.249	−0.489*	−0.408	−0.063	0.004	−0.172	1					
Ni	0.044	0.335	0.341	0.147	0.039	0.304	−0.531*	1				
Ba	−0.158	0.039	−0.107	0.189	0.751**	−0.123	−0.162	−0.057	1			
Ga	−0.017	0.127	0.097	−0.118	−0.228	−0.214	0.107	0.069	−0.204	1		
Ce	0.653**	0.576**	0.658**	0.146	−0.033	−0.189	−0.455*	0.068	−0.07	−0.192	1	
Sr	−0.303	−0.362	−0.460*	0.204	0.329	−0.079	0.401	−0.288	0.418	−0.139	−0.481*	1

*Correlation is significant at the 0.05 level (two-tailed), **Correlation is significant at the 0.01 level (two-tailed)

Table 10: Pearson correlation matrix of activity concentrations and major elements of Awba Dam sediments

	^{40}K	^{232}Th	^{238}U	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2
^{40}K	1											
^{232}Th	0.761**	1										
^{238}U	0.786**	0.939**	1									
SiO_2	−0.308	−0.086	−0.224	1								
Al_2O_3	0.133	0.35	0.357	−0.617**	1							
Fe_2O_3	0.149	−0.244	−0.161	−0.331	−0.382	1						
MnO	0.128	0.17	0.24	−0.399	0.502*	−0.132	1					
MgO	0.524*	0.471*	0.36	−0.18	0.116	−0.187	0.183	1				
CaO	0.364	0.469*	0.387	−0.24	0.553*	−0.277	0.670**	0.235	1			
Na_2O	0.585**	0.514*	0.447*	−0.094	0.307	−0.38	0.287	0.567**	0.523*	1		
K_2O	0.308	0.357	0.24	−0.217	0.324	−0.373	0.108	0.450*	0.327	0.646**	1	
TiO_2	0.344	0.614**	0.587**	−0.273	0.627**	−0.414	0.593**	0.257	0.721**	0.399	0.367	1

**Correlation is significant at the 0.01 level (two-tailed), *Correlation is significant at the 0.05 level (two-tailed)

REFERENCES

1. Hamilton-Taylor J, Kelly M, Kershaw P, Lambert CE. Radioecology after Chernobyl. 1993. p. 177-274. Available from: http://www.icsu.com/scopeorg/downloadpubs/scope50hapter05tml. [Last retrieved on 2008 Jul 15].
2. Isinkaye OM, Jibiri NN, Olomide AA. Radiological health assessment of natural radioactivity in the vicinity of Obajana cement factory, North Central Nigeria. J Med Phys 2015;40:52-9.
3. Omoniyi IM, Oludare SM, Oluwaseyi OM. Determination of radionuclides and elemental composition of clay soils by gamma- and X-ray spectrometry. Springerplus 2013;2:74.
4. Ghrefat H, Yusuf N. Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. Chemosphere 2006;65:2114-21.
5. Srinivasa Gowd S, Ramakrishna Reddy M, Govil PK. Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. J Hazard Mater 2010;174:113-21.
6. Olatunde MO, Farai IP, Awodugba AO. Natural radionuclide concentrations and radiological impact assessment of river sediments of the coastal areas of Nigeria. J Environ Prot 2011;2:418-23.
7. Bikit I, Varga E, Conkic Lj, Slivka J, Mrda D, Curcic S, *et al*. Radioactivity of the Bega sediment-case study of a contaminated canal. Appl Radiat Isot 2005;63:261-6.
8. Isinkaye MO, Oyedele EA. Assessment of radionuclides and trace metals in soil of an active designated municipal waste-dumpsite in Ado-Ekiti, Nigeria. J Int Environ Appl Sci 2014;9:402-10.
9. Emmanuel TT, Okorie T. Studies on the distribution and abundance of plankton in Awba stream and reservoir, University of Ibadan. Open J Ecol 2013;3:273-8.
10. Link DD, Kingston HM, Walter PJ. Development and validation of the new EPA microwave-assisted leach method 3051A. Environ Sci Technol 1998;32:3628-32.
11. Jibiri NN, Emelue HU. Soil radionuclide concentrations and radiological assessment in and around a refining and petrochemical company in Warri, Niger Delta, Nigeria. J Radiol Prot 2008;28:361-8.
12. UNSCEAR. Sources, ElTccts and Risks of Ionizing Radiation. United Nations Scientific Committee on the Effect of Atomic Radiation. Report to the General Assembly, with Annexes, New York: United Nations: 2000.
13. UNSCEAR. Sources and Effects of Ionizing Radiation. Report of the United Nations Scientific Committee on the Effects of Atomic Radiation to the General Assembly. (Annex B). New York: United Nations; 2008.
14. Nwankwo CU, Ogundare FO, Folley DE. Radioactivity concentration variation with depth and assessment of workers' doses in selected mining sites. J Radiat Res Appl Sci 2015;8:216-20.
15. Beretka J, Matthew PJ. Natural radioactivity of Australian building materials, industrial wastes and by-products. Health Phys 1985;48:87-95.
16. Jibiri NN, Okeyode IC. Activity concentrations of natural radionuclides in the sediments of Ogun river, Southwestern Nigeria. Radiat Prot Dosimetry 2011;147:555-64.
17. Jibiri NN, Temaugee ST. Radionuclide contents in raw minerals and soil samples and the associated radiological risk from some mining sites in Benue State North-Central Nigeria. Int J Sci Eng Res 2013;4:2392-400.
18. Xinwei L, Lingqing W, Xiaodan J, Leipeng Y, Gelian D. Specific activity and hazards of Archeozoic-Cambrian rock samples collected from the Weibei area of Shaanxi, China. Radiat Prot Dosimetry 2006;118:352-9.
19. NEA-OECD. Organisation for Economic Cooperation and Development Nuclear Energy Agency Report exposure to radiation from natural radioactivity in building materials. Paris, France: OECD; 1979.
20. Isinkaye MO, Farai IP. Activity concentrations of primordial radionuclides in sediments of surface water dams in Southwest Nigeria – A baseline survey. Radioprotection 2008;43:533-45.
21. Joshua EO, Oyebanjo OA. Distribution of heavy minerals in sediments of Osun river basin Southwestern, Nigeria. Res J Environ Earth Sci 2009;1:74-80.
22. Chowdhurry MI, Alam MN, Hazari SK. Distribution of

radionuclides in the rivers sediments and coastal soils of Chittagong, Bangladesh and evaluation of the radiation hazard. Appl Radiat Isot 1999;51:747-55.

23. Xinwei L, Xiaolan Z, Fengling W. Natural radioactivity in sediment of WEI river, China. Environ Geol 2008;53:1483-9.
24. El-Gamal A, Nasr S, El-Taher A. Study of spatial distribution of natural radioactivity in the Upper Egypt Nile river sediments. Radiat Meas 2007;42:457-65.
25. Khater AE, Ebaid YY, El-mongy SA. Distribution pattern of natural radionuclides in Lake Nasser bottom sediments. Int Congr Ser 2005;1276:405-6.
26. Narayana Y, Rajashekara KM, Siddappa K. Natural radioactivity in some major rivers of coastal Karnataka on the Southwest coast of India. J Environ Radioact 2007;95:98-106.
27. Ramasamy V, Murugesan S, Mullainathan S. Natural activity concentration and radiological hazards of Pala river sediment Tamil Nadu, India. The Indian Mineralogist 2006;40:9-23.
28. Qureshi AA, Tariq SA, Ud Din K, Manzoor S, Calligaris, Waheed A. Evaluation of excessive lifetime cancer risk due to natural radioactivity in the rivers sediments of Northern Pakistan. J Radiat Res Appl Sci 2014;7:438-47.
29. Kobya Y, Taskin H, Yeslkanat CM, Varinlioglu A, Korcak S. Natural and artificial radioactivity assessment of dam lakes sediments in Coruh river, Turkey. J Radioanal Nucl Chem 2015;303:287-95.
30. Eroglu H, Kabadayi Ö. Natural radioactivity levels in lake sediment samples. Radiat Prot Dosimetry 2013;156:331-5.
31. Farai IP, Isinkaye MO. Radiological safety assessment of surface-water dam sediments used as building material in Southwestern Nigeria. J Radiol Prot 2009;29:85-93.
32. Jibiri NN, Okeyode IC. Evaluation of radiological hazards in the sediments of Ogun river, Southwestern Nigeria. Radiat Phys Chem 2012;81:103-12.
33. Turekian KK, Wedepohl KH. Distribution of elements in some major units of the earth's crust. Geol Soc Am Bull 1961;72:175-92.
34. Rezaee KH, Saion EB, Yap CK, Abdi MR, RiyahiBakhtiari A. Vertical distribution of heavy metals and enrichment in the South China Sea sediment cores. Int J Environ Res 2010;4:877-86.
35. Simex SA, Helz GR. Regional geochemistry of trace elements in Checapeake Bay. Environ Geol 1981;3:315-23.
36. Taylor SR, McLennan SM. The geochemical evolution of the continental crust. Rev Geophys 1995;33:224-65.
37. Sutherland RA. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ Geol 2000;39:611-27.
38. Habes G, Yousef AR, Marc AR. Hydrogeological data evaluation and solid waste management at Al-Akeeder landfill site, Jordan: Assessing Pollution Risks. Int J Ecol Environ Sci 2010;36:175-86.
39. Müller G. Index of geoaccomulation in sediments of the Phine river. Geol J 1969;2:109-18.