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Natural radionuclides and ions concentrations in water and sediments around iron-smelting industry in Ikirun, Osun-State, Nigeria

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ABSTRACT: Natural radionuclides pose a threat to the environment, because of the radioactivity they undergo. Water is said to be the sink of all pollutants including radionuclides and water pollution is a serious challenge due to the direct link between the adequacy of good quality water and the state of public health. The concentrations of uranium-238, thorium-232 and potassium-40 and ions in the selected water bodies around Ikirun Iron-smelting Industry were determined in wet and dry seasons to highlight possible radioactive pollution from the iron-smelting emissions. The radionuclides were analyzed using gamma spectroscopy. It was observed that ^{238}U, ^{232}Th, and ^{40}K had their calculated annual effective dose (0.00004, 0.00003, and 0.010 $mSvyr^{-1}$) to be below the WHO individual dose criterion of 0.1 $mSvyr^{-1}$ and reference level of 1 $mSvyr^{-1}$ in drinking water. The mean activity concentrations (AC) of U-238, Th-232 and K-40 in water were observed to be higher in the wet season (3.84±0.6, 2.37±0.5 and 15.83±1.3 $Bqkg^{-1}$ respectively) than in the dry season (2.81±0.00, 0.92±0.00, and 10.2±0.00 $Bqkg^{-1}$ respectively). The radionuclides, ^{238}U, ^{232}Th, and ^{40}K also had their AC higher in sediment (40.50 ± 10.50, 66.24 ± 13.50 and 340.22 ± 9.00 BqL^{-1}; $Bqkg^{-1}$) than in water (1.28 ± 0.30, 0.26 ± 0.10 and 5.75 ± 0.70 $Bqkg^{-1}$). The range of AC for ^{232}Th, ^{238}U, and ^{40}K in water are 0.17 - 2.49 $Bqkg^{-1}$, 1.01 - 4.04 $Bqkg^{-1}$, and 3.98 - 17.48 $Bqkg^{-1}$ respectively with ^{40}K having the highest AC throughout the sampling locations. The result of anions in water samples for the sampling period are in the decreasing order of Cl^{-} (3.55 - 106.95 mgL^{-1}) < SO_4^{2-} (0.25 - 15.82 mgL^{-1}) < NO_3^{-} (0.01 - 0.49 mgL-1) while cations in water samples for the sampling period are in increasing order of Na^{+} (0.054 - 0.212 mgL^{-1}) < Mg^{2+} (0.066 - 0.282mgL^{-1}) < Ca^{2+} (0.077 -0.261mgL^{-1}) < K^{+} (0.40-3.1 mgL^{-1}), with potassium having the highest concentration range. The study observed no significant radionuclides pollution of water and sediment in the study area.

Keywords: ^{40}K, ^{232}Th, ^{238}U, activity concentration, annual effective dose, radioactivity, water pollution.

INTRODUCTION

Environmental pollution is a major challenge in Africa which includes Nigeria. Water is said to be the sink of all pollutants including radionuclides in the environment and water pollution is a serious challenge due to the direct link between the adequacy of good quality water and the state of public health (Okoya et al., 2020a). Karahan et al. (2020) and Ugbede et al. (2020) observed that the ever-growing industrialization which includes Iron-Smelting without proper emission control or pollution moderation has given rise to increasing environmental pollution, especially air and water pollution and global health issues associated to radionuclides and trace metals which may have grievous effect on human wellbeing especially when they find their ways into food chain (Okoya et al., 2011; ATSDR, 1999; ATSDR, 2011).

Radionuclides are atoms that have excess nuclear energy therefore rendering it unstable and they often have half-life range of mere seconds to half-life of hundreds or millions of years (Karahan et al., 2020). They can undergo radioactivity which involves nuclear disintegration of the unstable nuclides to achieve a more stable configuration and this is accompanied by the emission of ionizing radiation. Radioactive elements occur both naturally and through anthropogenic activities, hence, human beings are exposed to radiation through both sources (ATSDR 1999; ATSDR 2011). Some radionuclides such as the primordial nuclides of uranium-238, thorium-232, and potassium-40 have been in existence since the formation of the universe and are often referred to as naturally occurring radionuclides (Omale et al., 2014). An average radioactive dose of about 2.4 mSv/y has been estimated globally from natural sources (Pintilie-Nicolov et al., 2020), which is independent of whether the exposure is external, that is, direct radiation or internal, which could be by ingestion or inhalation (Ilaria et al., 2021). The level of radiation is also independent of the source of the environmental pollution. However, the absorbed dose of the radiation determines the effect on humans. High radiation dose may alter the DNA of human while low dose may have no appreciable effect (Oluyide et al., 2019). Omale et al. (2014) observed that the mobility of the radionuclide in soil systems determines their transport in hydro biological systems and their transfer into streams, surface water bodies and ground water. The soil on the earth's crust pose a great threat as it aids mobilization and transportation of radionuclides, however, water forms the reservoir for the radionuclides. This is because the soil is constantly in contact with the population and it allows seepage or leaching of dissolved radionuclides into water bodies and sediment, thus taken up by aquatic lives and also uptake by plants from soil, water and sediments. Therefore, radionuclides enter food chain through plants and water and contaminate humans by ingestion (Ilaria et al., 2021). Geologically, the radionuclide concentration of the environment is dependent on the location and Ilaria et al. (2021) opined that this is because the distribution of naturally occurring radionuclides is due to the distribution of the rocks they originated from and their concentration processes. According to United States Environmental Protection Agency (2008), 80% of human exposure to radiation occurs naturally and varies according to factors such as individual's location, lifestyle, occupation and daily activities despite the fact that radiation are extremely harmful to living organisms including man. Human exposure to these radiation lead to cancer, birth defects and other acute illness in human (ATSDR, 1999; ATSDR, 2011). Radiation affects the biota based on the type of radiation (α, β, ɣ), the energy of radiation, the level of activity (distribution per unit time), the nuclides chemical and physical properties of the contaminated material and surrounding as well as properties relating to the species. Therefore, radionuclides pose a threat when present in the environment, because of the radioactivity they undergo (USEPA, 2008).

It was observed that the water bodies around the Ikirun Iron-Smelting are used for domestic and agricultural purposes by people in Ikirun and its environments as the water also flows into communities around Ikirun town thus making it essential to constantly analyse the effect of the emissions on the water bodies in this environment. This study therefore assessed the level of the natural radionuclides and ionic contents in the said water bodies as a means of evaluating the effect of the emissions from the Iron-Smelting industry on the water and sediments in this environment.

MATERIALS AND METHODS

Description of sampling locations

The Iron Smelting industry is situated in Ikirun town in Ifelodun Local Government Area of Osun State and there are no other industrial developments within the area. Ikirun is situated in the north-eastern part of Osun State, South-western Nigeria. The study area covers an aerial extent of about 6.0 km^2 (Figure 1).

Sampling

The sampling points were randomly selected within a radius of 2.40 km from the industry (Figure 1, Table 1). Samplings were conducted bimonthly cutting through the wet and dry season of one year. Seventy-two water samples and sixty sediment samples were collected from seven sampling points along the stream, two from two hand dug wells, and three from three ponds every two months for one year. The water samples were acidified with 10mL of 11M hydrochloric acid per litre. Sediment samples were collected into polythene bags from all sampling points except the wells.

Determination of radionuclides in the samples

The radionuclides were determined in the samples using gamma spectrometry. The water sample was first filtered and acidified to a pH of 2. Marinelli beakers of 1 litre volume capacity were then filled with known volume of the various water samples and 1.2 kg of sieved sediment and later firmly sealed for 30 days. The Gamma-counting equipment used was a Canberra sodium iodide thallium activated crystal detector and the analysis was carried out at the Center for Energy Research and Development (CERD), Obafemi Awolowo University (OAU), Ife. The Activity Concentrations (AC) of K-40 was determined by direct gamma-spectrometry at 1460.8 keV while the ACs of U-238 and Th-232 were determined through their "daughters". The gamma spectroscopy analysis was carried out by spectra-analysis program, SAMPO 90 which matched gamma-energies to a group of possible isotopes at various energy levels. Triplicate analyses were conducted on the water samples (Nwankwo (2013). The ACs recorded was converted to the annual effective dose (AED) of radionuclide in human body. The AED per person for radionuclides is given by:

$$AED = \Sigma I_i . 365 \cdot D_i$$

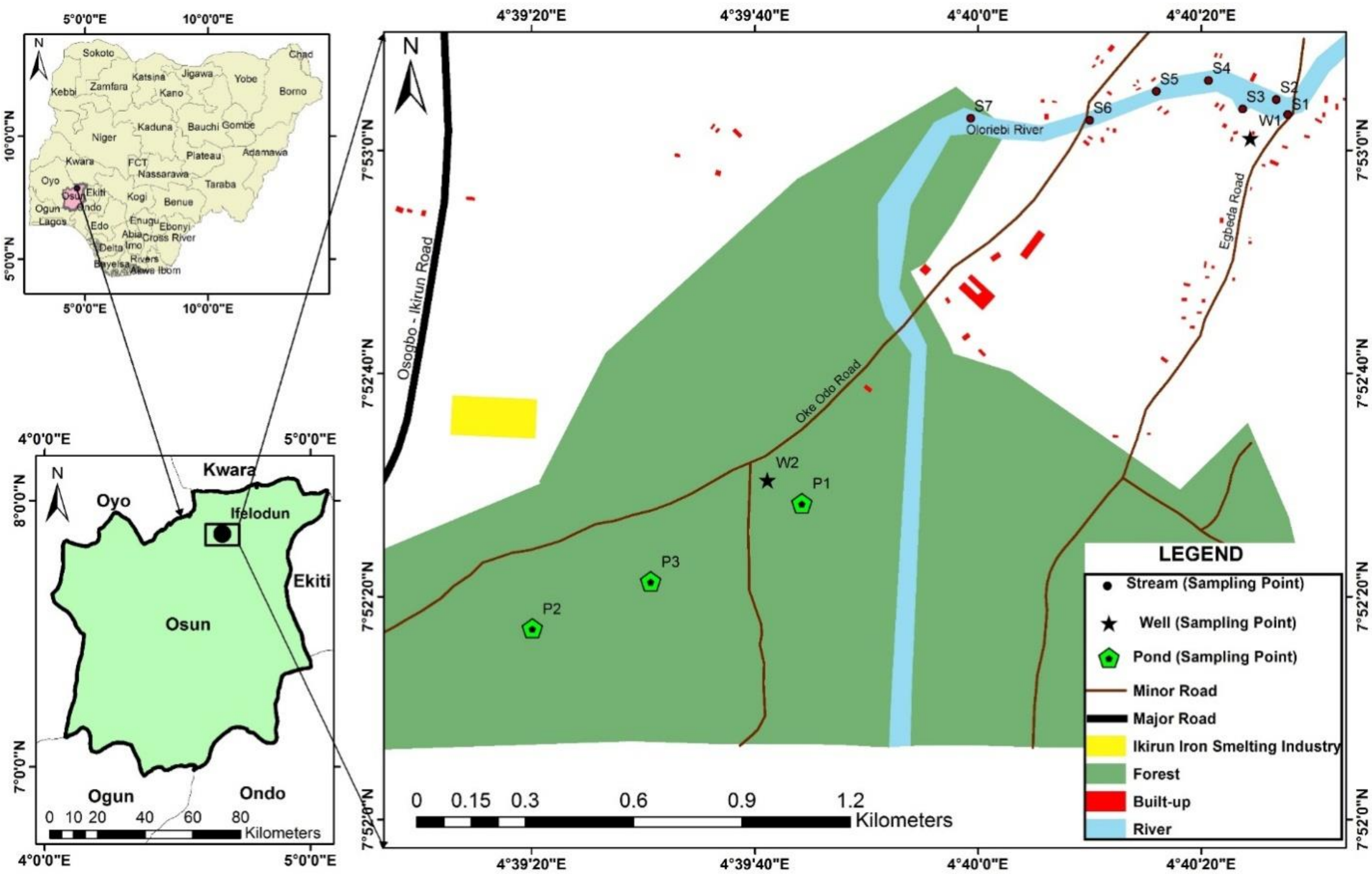

Figure 1. Location of sampling points in Ifelodun Local Government Area of Osun State.

Table 1. The geographical locations of the sampling stations.

S/N	Sampling points	Grid coordinates		Elevation (m)	Distance from Ikirun iron smelting industry (km)
		Northing	Easting		
1	Stream 1	7.884220°	4.674370°	395	2.37
2	Stream 2	7.884596°	4.674087°	388	2.33
3	Stream 3	7.884360°	4.673250°	383	2.25
4	Stream 4	7.885070°	4.672400°	385	2.18
5	Stream 5	7.884800°	4.671100°	386	2.05
6	Stream 6	7.884080°	4.669440°	380	1.83
7	Stream 7	7.884130°	4.666480°	377	1.57
8	Well 1	7.883633°	4.673438°	392	2.23
9	Well 2	7.875120°	4.661418°	380	0.78
10	Pond 1	7.874550°	4.662280°	378	0.88
11	Pond 2	7.871430°	4.655570°	388	0.58
12	Pond 3	7.872604°	4.658519°	392	0.63

Where I_i is the daily intakes of radionuclide I (Bqd^{-1}) which is equivalent to the AC ($Bqkg^{-1}$), assuming the daily intake value is 1 liter and D_i is the ingestion dose coefficient for each radionuclide (Table 2).

Determination of the cationic content of the samples

Cationic content (Na^+, K^+, Ca^{2+}, and Mg^{2+}) in the samples were determined using Flame Emission Spectrophoto-

Table 2. Annual effective dose of ^{238}U, ^{232}Th and ^{40}K in Water Samples.

Radionuclides	Ingested dose factor (Sv yr^{-1})	Concentrations/ unit	Stream	Pond 1	Pond 2	Pond 3	Well 1	Well 2
U-238	1.1×10^{-10}	AC (Bqkg^{-1})	2.35±0.12	1.34±0.12	1.13±0.08	1.13±0.05	3.41±0.23	3.02±0.21
		AED (mSv yr^{-1})	0.00009	0.00005	0.00004	0.00004	0.00013	0.00012
Th-232	4.3×10^{-10}	AC (Bqkg^{-1})	1.12±0.05	0.78±0.04	0.34±0.02	0.21±0.02	2.13±0.12	0.98±0.05
		AED (mSv yr^{-1})	0.00017	0.00012	0.00005	0.00003	0.00033	0.00015
K-40	6.2×10^{-9}	AC (Bqkg^{-1})	10.31±0.82	7.92±0.70	4.99±0.32	4.40±0.36	12.70±1.41	11.48±1.27
		AED (mSv yr^{-1})	0.023	0.018	0.011	0.010	0.029	0.026

NB: AC = Activity Concentration, AED = Annual Effective Dose.

Table 3. Seasonal variations in the mean (± SE) concentrations of radionuclides of surface and ground water.

Water parameters	Surface water								P-value	T-value	Ground water				P-value	T-value
	Wet Season				Dry Season						Wet Season		Dry Season			
	stream	pond 1	pond 2	pond 3	Stream	pond 1	pond 2	pond 3			well 1	well 2	well 1	well 2		
U-238 (Bqkg^{-1})	2.73±0.70	1.63±0.40	1.34±0.40	1.28±0.30	2.23±0.15	1.24±0.15	1.06±0.20	1.09±0.25	0.015	5.059	3.84±0.60	3.41±0.60	3.17±0.00	2.81±0.00	0.152	2.265
Th-232 (Bqkg^{-1})	1.29±0.40	0.91±0.50	0.40±0.10	0.26±0.10	1.08±0.24	0.74±0.11	0.32±0.09	0.20±0.09	0.036	3.629	2.37±0.50	1.09±0.40	2.01±0.00	0.92±0.00	0.782	0.315
K-40 (Bqkg^{-1})	13.37±0.90	10.43±1.00	6.14±0.70	5.75±0.70	9.49±0.90	7.23±0.45	4.74±0.15	4.04±0.10	0.023	4.296	15.80±1.30	14.28±1.70	11.28±0.00	10.20±0.00	0.044	4.612

NB: Using sig 0.01 and 0.05 (99% and 95% confidence), significance values below 0.01 are very significant, significance values below 0.05 are significant, significance values above 0.05 are not significant.

meter as recorded by APHA et al. (1999).

Determination of the anionic content of the samples

The anionic content (NO_3^-, SO_4^{2-}) of the samples were determined according to standard methods by APHA et al. (1999) while Cl^- was determined by method described by Golterman et al. (1978).

RESULTS AND DISCUSSION

Analysis of radionuclide in water

There were high significant differences for the selected radionuclides ($p<0.01$) among the sampling locations. For the sampling period, the range of AC of ^{232}Th, ^{238}U, and ^{40}K were 0.17 to 2.49, 1.01 to 4.04, and 3.98 to 17.48 Bqkg^{-1} respectively with ^{40}K having the highest AC throughout the sampling locations. This trend of ^{40}K having the highest AC is in accordance with the research of Nwankwo (2013), Omale et al. (2014) and Ugbede et al. (2020) carried out in different areas in Nigeria. High levels of ^{40}K and K^+(Tables 2 and 3) detected could be a function of the geological formation of the area more so that Ugbede et al. (2020) earlier reported ^{40}K as the major naturally occurring source of internal radiation despite its low isotopic abundance.

Uranium-238, Potassium-40, and Thorium-232 have their highest mean AC in the well water sample (3.41±0.24, 12.70±1.42, and 2.13±0.12 Bqkg^{-1} respectively). This observation is similar to the findings of Thabayneh et al. (2012) in natural water resources in Hebron Province, Palestine and also Oluyide et al. (2018) who recorded highest level of K-40 in borehole followed by well water and the least concentration in streams in his study around the steel smelting industry in Ile-Ife, Nigeria. This finding can be attributed to the depth of wells compared to surface water where the radionuclides could easily settle into the sediment. However, the observation contradicts the findings of Hu et al. (2021) who discovered decrease in the concentra-

Table 4. Comparison of the mean concentration of the selected water parameters with NIS and WHO standards.

Parameters	Stream	Pond 1	Pond2	Pond 3	Well 1	Well 2	WHO Standard	NIS Standard
238U (mSv yr^{-1})	0.00009	0.00005	0.00004	0.00004	0.00013	0.00012	0.1	0.1
232Th (mSv yr^{-1})	0.00017	0.00012	0.00005	0.00003	0.00033	0.00015	0.1	0.1
40K (mSv yr^{-1})	0.023	0.018	0.011	0.010	0.029	0.026	0.1	0.1
K^+ (mgL^{-1})	0.96	1.07	1.59	1.81	0.94	0.93	-	-
Na^+ (mgL^{-1})	0.14	0.26	0.16	0.17	0.18	0.16	200	200
Ca^{2+} (mgL^{-1})	0.15	0.13	0.17	0.18	0.16	0.18	7.5	7.5
Mg^{2+} (mgL^{-1})	0.13	0.16	0.16	0.16	0.17	0.20	-	0.2
SO_4^{2-} (mgL^{-1})	12.57	11.16	12.50	14.30	10.61	15.12	500	100
NO_3^- (mgL^{-1})	0.14	0.14	0.13	0.12	0.19	0.14	50	50
Cl- (mgL^{-1})	77.67	38.80	59.73	80.30	13.79	91.98	250	250

tion of Thorium as depth increases in his study about the impact of thorium caused by mining.

In Table 3, the mean AC of U-238, Th-232 and K-40 are higher in the wet season (2.73±0.7, 1.29±0.4 and 13.37±0.9 $Bqkg^{-1}$ respectively) than in the dry season (1.06±0.2, 0.2±0.09, and 4.04±0.1 $Bqkg^{-1}$ respectively). These observations could be as a result of constant mixing of the surface water as a result of rainfall which gives limited opportunity for the radionuclides to re-suspend in sediments of the stream unlike in dry season where the water volume is reduced and the water settled.

However, higher mean AC of U-238, Th-232 and K-40 (3.84±0.6, 2.37±0.5 and 15.83±1.3 respectively) were recorded in ground water than the surface water values of 1.06±0.2, 0.2±0.09, and 4.04±0.1 $Bqkg^{-1}$ respectively (Table 3). This trend could be as a result of the geological formation of the area, since these radionuclides could also be naturally present in the area. The mean AC of the three radionuclides, U-238, Th-232 and K-40, are all significantly different ($p<0.05$) between the seasons in surface water but not significantly different in ground water except for K-40 which could be due to internal radiation sources apart from being due to geological formation. Meanwhile, the mean annual effective dose (AED) per person for all the radionuclides in stream, pond 1, pond 2, pond 3, well 1 and well 2 are U-238 (0.00009, 0.00005, 0.00004, 0.00004, 0.00013, and 0.00012 mSv yr^{-1} respectively), Th-232 (0.00017, 0.00012, 0.00005, 0.00003, 0.00033, and 0.00015 mSv yr^{-1} respectively) and K-40 (0.023, 0.018, 0.011, 0.010, 0.029, and 0.026 mSv yr^{-1} respectively) (Table 4). These AED are all below the WHO recommended level of 0.1 $mSvy^{-1}$ for drinking water and also below the tolerable level of 1 $mSvy^{-1}$ to the general public for prolonged exposure as recommended by the International Commission on Radiological Protection (ICRP, 2000; WHO, 2011) (Table 4).

Ions in the water samples

The results of anions obtained from the water sample for the sampling period ranged NO_3^- (0.01 to 0.49), SO_4^{2-} (0.25 to 17.91) and Cl^- (3.55 to 106.5) mgL^{-1}. There was no significant difference in the concentrations of $SO_4^{2-}$and NO_3^- among the sampling locations during the sampling period. The mean concentrations of anions obtained are all below the maximum permissible limit for both WHO and NIS (Table 4) (WHO, 2006; NIS, 2007).

The result of cations in water samples for the sampling period are in the increasing order of Na^+ (0.054 to 0.212 mgL^{-1}) < Mg^{2+} (0.066 to 0.282 mgL^{-1}) < Ca^{2+} (0.077 to 0.261 mgL^{-1}) < K^+ (0.40 to 3.1 mgL^{-1}). The mean concentration of Magnesium ion is higher in well 2 (0.20±0.03) mgL^{-1} and lowest in stream (0.13±0.02) mgL^{-1}. The mean concentration of calcium ion is higher in pond 3 (0.18±0.02) mgL^{-1} and lowest in pond 1 (0.13±0.03) mgL^{-1} and there was no significant difference among the sampling locations for both Mg^{2+} and Ca^{2+}, this is in accordance with the results of Ugbede et al. (2020).

For K^+, highest mean concentration was recorded in pond 3 (1.81±0.51 mgL^{-1}) and lowest in well 2 (0.93±0.37 mgL^{-1}) with no significant difference among the sampling locations. In this study, K^+ has the highest concentration among the observed cations. This could be because of use of NPK fertilizer on farm site, constant washing with soap around the sampling locations, domestic effluent runoff which could include urine and other anthropogenic sources. It could also be as a result of geological formation of the study area, as the soil type of Ikirun is said to be coarse grain nice which is rich in potassium (Olayiwola, 2013).

In ground water, the lowest and highest mean

Table 5. Seasonal variations in the mean (± SE) concentrations of ions of surface and ground water collected.

Water parameters	Surface water								P-value	T-value	Ground water				P-value	T-value
	Wet season				Dry season						Wet season		Dry season			
	stream	pond 1	pond 2	pond 3	Stream	pond 1	pond 2	pond 3			well 1	well 2	well 1	well 2		
Mg^{2+} (mgL^{-1})	0.15±0.00	0.18±0.00	0.18±0.00	0.17±0.00	0.12±0.03	0.14±0.04	0.13±0.03	0.14±0.04	0.009	6.117	0.17±0.00	0.20±0.00	0.18±0.02	0.19±0.04	0.791	0.302
Cl^- (mgL^{-1})	86.89±8.49	59.17±26.03	55.62±26.11	92.30±7.10	68.46±1.16	18.43±8.05	63.83±4.73	68.30±1.48	0.162	1.845	11.45±6.71	92.30±8.20	17.30±12.80	91.50±9.4	0.967	0.046
Ca^{2+} (mgL^{-1})	0.17±0.00	0.10±0.00	0.17±0.00	0.19±0.00	0.13±0.01	0.16±0.05	0.16±0.01	0.17±0.03	0.876	0.170	0.16±0.00	0.16±0.00	0.15±0.04	0.21±0.02	0.680	0.478
SO_4^{2-} (mgL^{-1})	12.99±1.24	11.63±2.32	12.33±1.76	14.30±0.12	12.14±0.98	10.70±2.21	12.67±1.57	14.30±0.12	0.335	1.146	10.16±4.97	16.40±0.81	11.28±2.10	13.20±1.22	0.780	0.319
NO_3^- (mgL^{-1})	0.12±0.05	0.12±0.05	0.11±0.05	0.10±0.05	0.16±0.01	0.17±0.04	0.14±0.01	0.14±0.01	0.002	9.798	0.23±0.14	0.13±0.04	0.14±0.01	0.14±0.03	0.485	0.849
Na^+ (mgL^{-1})	0.15±0.00	0.11±0.00	0.16±0.00	0.17±0.00	0.13±0.02	0.42±0.28	0.16±0.03	0.17±0.02	0.429	0.913	0.17±0.00	0.15±0.00	0.20±0.02	0.17±0.02	0.352	1.205
K^+ (mgL^{-1})	1.08±0.00	0.90±0.00	1.67±0.00	1.52±0.00	0.80±0.21	1.25±0.91	1.52±0.56	2.09±0.77	0.589	0.603	1.10±0.00	0.75±0.01	1.26±0.06	1.57±0.57	0.172	2.086

NB: Using sig 0.01 and 0.05 (99% and 95% confidence), significance values below 0.01 are very significant, significance values below 0.05 are significant, significance values above 0.05 are not significant.

concentration of Mg^{2+} and NO_3^- were recorded in wet season. However, in surface water, the mean concentration of Mg^{2+} in the wet season is higher (0.18±0.00) mgL^{-1} than in dry season (0.12±0.03) mgL^{-1} while the concentration of NO_3^- in the dry season is higher (0.17±0.04) mgL^{-1} than in wet season (0.10±0.05) mgL^{-1} (Table 5). The values of Mg^{2+} and NO_3^- in wet season for surface water are significantly different ($p<0.01$) from that of dry season while their values are not significantly different in ground water. However, the mean concentrations values for Chloride, Nitrate, Sodium, Sulphate, and Magnesium ions in surface and underground water were below the Nigerian Standards for drinking water quality and WHO standards (WHO, 2006; NIS, 2007) (Table 4).

Sediment samples analysis

During this study, the Cl^-, NO_3^- and SO_4^{2-} values obtained ranged from 13.69 to 37.78 $mgkg^{-1}$, 3.77 to 21.91 $mgkg^{-1}$, and 10.13 to 42.84 $mgkg^{-1}$ respectively. The mean concentrations of anions in sediments are in the decreasing order of SO_4^{2-}>Cl^->NO_3^-. The mean concentration of Cl^-, and SO_4^{2-} are both highest in pond 2 (32.82±1.8 and 32.83±3.81 $mgkg^{-1}$ respectively) and lowest in pond 3 (24.57±3.40 and 23.60±4.78 $mgkg^{-1}$ respectively) compared with other locations. However, the mean concentration of NO_3^- is highest in pond 1 (16.09±2.72 $mgkg^{-1}$) and lowest in the stream (12.19±0.90 $mgkg^{-1}$) within the sampling locations. The cations concentration in sediments are in the decreasing order of K^+> Ca^{2+}> Na^+> Mg^{2+}. The values of K^+, Ca^{2+}, Na^+ and Mg^{2+} obtained during the study ranged from 0.068 to 1.62, 0.023 to 0.177, 0.007 to 0.16, and 0.008 to 0.12 $mgkg^{-1}$ respectively. Pond 2 has the highest mean concentration of both Mg^{2+} (0.064±0.021) and Na^+ (0.073±0.027) $mgkg^{-1}$ while the stream has the lowest mean concentration for both Mg^{2+}(0.053±0.019) and Na^+(0.069±0.026) $mgkg^{-1}$ within the sampling locations. The mean concentration of Ca^{2+} is highest in pond 1 (0.112±0.032) $mgkg^{-1}$ and lowest in pond 3 (0.065±0.018) $mgkg^{-1}$ while the mean concentration of K^+ is highest in pond 3 (0.781±0.296) $mgkg^{-1}$ and lowest in pond 2 (0.411±0.142) $mgkg^{-1}$ within the sampling locations. The values of the ions obtained in the study are generally high in the pond which is in accordance with the report of Okoya et al. (2020b) in a similar study but different locations.

The Uranium-238, Thorium-232, and Potassium-40 values obtained in sediment during the sampling period ranged from 19.94 to 70.1, 36.62 to 107.04, and 10.56 to 783.75 ($Bqkg^{-1}$) respectively. The mean AC of ^{238}U and ^{232}Th are both highest in pond 1 (44.73±13.34 and 88.64±9.20 $Bqkg^{-1}$ respectively) but both ^{238}U and ^{40}K are lowest in pond 2 (36.09±4.71 and 322.28±178.63 $Bqkg^{-1}$ respectively). However, the mean AC of ^{232}Th is lowest in the stream (73.37±6.69 $Bqkg^{-1}$) while the mean AC of ^{40}K is highest in the stream (649.535±37.477 $Bqkg^{-1}$). High AC of these radionuclides in sediment could be due to the process of deposition and re-suspension of the radionuclides in sediment from water (Omale et al., 2014; Kemker, 2014).

In this study, cations in sediment samples are significantly high in dry season than in wet season, this could be as result of constant runoff washing away the nutrients in wet season. The mean concentration of Mg^{2+}, Ca^{2+}, K^+ and Na^+ are highest in dry season (0.088±0.00, 0.133±0.01, 1.144±0.00 and 0.097±0.0011 $mgkg^{-1}$ respectively) and lowest in wet season (0.019±0.00, 0.048±0.00, 0.15±0.00 and 0.015±0.00 $mgkg^{-1}$ respectively) (Table 6). However, the mean value for Ca^{2+}, Mg^{2+} and Na^+ in wet and dry seasons are significantly different

Table 6. Seasonal variations in the mean (± SE) Concentrations of the Radionuclides and Ions for sediment samples in Ikirun environs.

Water parameters	Wet season				Dry season				P-value	T-value
	Stream	Pond 1	Pond 2	Pond 3	Stream	Pond 1	Pond 2	Pond 3		
Cl^- (mgkg^{-1})	24.36±2.13	25.25±0.00	33.27±2.87	29.11±1.55	29.18±1.39	28.37±5.26	32.38±2.81	20.04±5.90	0.88	-0.164
Mg^{2+} (mgkg^{-1})	0.05±0.00	0.02±0.00	0.04±0.00	0.04±0.00	0.06±0.02	0.07±0.00	0.09±0.00	0.073±0.00	0.03	3.889
Ca^{2+} (mgkg^{-1})	0.07±0.00	0.05±0.00	0.06±0.00	0.05±0.00	0.11±0.04	0.13±0.01	0.11±0.00	0.078±0.00	0.02	4.239
SO_4^{2-} (mgkg^{-1})	28.26±2.10	20.16±0.00	33.43±6.62	26.18±5.11	25.39±1.14	29.40±6.75	32.22±5.34	21.02±9.10	1.00	0.000
NO_3^- (mgkg^{-1})	12.48±1.83	11.98±0.00	15.07±1.72	18.04±1.41	11.90±0.78	17.45±3.33	14.75±1.02	8.52±4.12	0.72	-0.399
Na^+ (mgkg^{-1})	0.06±0.00	0.02±0.00	0.05±0.00	0.05±0.01	0.08±0.03	0.09±0.00	0.097±0.00	0.096±0.00	0.02	4.704
K^+ (mgkg^{-1})	0.50±0.00	0.15±0.00	0.40±0.00	0.42±0.00	0.47±0.20	0.67±0.00	0.43±0.00	1.144±0.00	0.19	1.682
Uranium-238 (BqL^{-1}; Bqkg^{-1})	40.45±10.15	70.10±15.00	38.14±10.00	40.50±10.50	34.78±14.80	32.05±7.50	34.04±5.50	41.27±6.00	0.28	-1.326
Thorium-232 (BqL^{-1}; Bqkg^{-1})	79.29±15.00	107.04±17.00	94.54±14.00	66.24±13.50	67.46±9.55	79.45±19.00	55.67±11.50	84.07±13.00	0.31	-1.229
Potassium-40 (BqL^{-1}; Bqkg^{-1})	648.87±9.80	514.14±10.00	260.56±9.50	340.22±9.00	650.21±89.67	236.30±3.00	384.01±3.00	503.2±6.50	0.98	0.025

NB: Using sig 0.01 and 0.05 (99% and 95% confidence), significance values below 0.01 are very significant, significance values below 0.05 are significant, significance values above 0.05 are not significant.

Table 7. Correlation in the mean (± SE) concentration of the selected radionuclides and ions from water and sediment samples in wet season.

Parameters	Water				Sediment				P-value	R-value
	Stream	Pond 1	Pond 2	Pond 3	Stream	Pond 1	Pond 2	Pond 3		
Cl^- (mgL^{-1}; mgkg^{-1})	86.89±8.49	59.17±26.03	55.62±26.11	92.30±7.10	24.36±2.13	25.25±0.00	33.27±2.87	29.11±1.55	0.639	0.361
Mg^{2+}(mgL^{-1}; mgkg^{-1})	0.15±0.00	0.18±0.00	0.18±0.00	0.17±0.00	0.05±0.00	0.019±0.00	0.041±0.0013	0.04±0.00	0.302	0.698
Ca^{2+} (mgL^{-1}; mgkg^{-1})	0.17±0.00	0.10±0.00	0.17±0.00	0.19±0.00	0.07±0.00	0.048±0.00	0.056±0.0015	0.051±0.00	0.630	0.37
SO_4^{2-} (mgL^{-1}; mgkg^{-1})	12.99±1.24	11.63±2.32	12.33±1.76	14.30±0.12	28.26±2.10	20.16±0.00	33.43±6.62	26.18±5.11	0.787	0.213
NO_3^- (mgL^{-1}; mgkg^{-1})	0.12±0.05	0.12±0.05	0.11±0.05	0.10±0.05	12.48±1.83	11.98±0.00	15.07±1.72	18.04±1.41	0.003	0.997
Na^+ (mgL^{-1}; mgkg^{-1})	0.15±0.00	0.11±0.00	0.16±0.00	0.17±0.00	0.057±0.00	0.02±0.00	0.049±0.0015	0.05±0.01	0.126	0.874
K^+ (mgL^{-1}; mgkg^{-1})	1.08±0.00	0.90±0.00	1.67±0.00	1.52±0.00	0.503±0.00	0.15±0.00	0.396±0.0018	0.42±0.00	0.515	0.485
U-238 (Bqkg^{-1}; BqL^{-1})	2.73±0.70	1.63±0.40	1.34±0.40	1.28±0.30	40.45±10.15	70.1±15.00	38.14±10.00	40.50±10.50	0.919	0.081
Th-232 (Bqkg^{-1}; BqL^{-1})	1.29±0.40	0.91±0.50	0.40±0.10	0.26±0.10	79.29±15.00	107.04±17.00	94.54±14.00	66.24±13.50	0.741	0.259
K-40 (Bqkg^{-1}; BqL^{-1})	13.37±0.90	10.43±1.00	6.14±0.70	5.75±0.70	648.87±9.80	514.14±10.00	260.56±9.50	340.22±9.00	0.027	0.973

NB: Using sig 0.01 and 0.05 (99% and 95% confidence), significance values below 0.01 are very significant, significance values below 0.05 are significant, significance values above 0.05 are not significant.

($p<0.05$). Also, high level of chloride ion was recorded in dry season (29.18±1.39) than in wet season (24.36±2.13) and this could be as a result of dilution of the said ions in water during the wet season (Ugbaja and Ephraim 2019; Okoya et al., 2020b) (Table 6).

Correlation between the concentration of radionuclides and ions in water and sediment

The mean concentrations of Cl^-, Na^+, Mg^{2+}, Ca^{2+}, and K^+ are higher in water than in sediment throughout the sampling period. Meanwhile, the mean concentration of SO_4^{2-}, NO_3^-, U-238, Th-232 and K-40 are all higher in sediment throughout the sampling period (Tables 7 and 8). However, the highest concentration of K-40 was recorded in surface water for both sediment and water and K-40 was discovered to have the highest concentration

Table 8. Correlation in the mean (± SE) concentration of the selected radionuclides and ions from water and sediment samples in dry season.

Water parameters	Water				Sediment				P-value	R-value
	Stream	Pond 1	Pond 2	Pond 3	Stream	Pond 1	Pond 2	Pond 3		
Cl^- (mgL^{-1}; $cmol\ kg^{-1}$)	68.46±1.16	18.43±8.05	63.83±4.73	68.30±1.48	29.18±1.39	28.37±5.26	32.38±2.81	20.04±5.90	0.830	0.170
Mg^{2+} (mgL^{-1}; $mgkg^{-1}$)	0.12±0.03	0.14±0.04	0.13±0.03	0.14±0.04	0.06±0.02	0.07±0.00	0.09±0.00	0.07±0.00	0.432	0.568
Ca^{2+} (mgL^{-1}; $mgkg^{-1}$)	0.13±0.01	0.16±0.05	0.16±0.01	0.17±0.03	0.11±0.04	0.13±0.01	0.11±0.00	0.08±0.00	0.732	0.268
SO_4^{2-} (mgL^{-1}; $mgkg^{-1}$)	12.14±0.98	10.70±2.21	12.67±1.57	14.30±0.12	25.39±1.14	29.40±6.75	32.22±5.34	21.02±9.10	0.374	0.626
NO_3^- (mgL^{-1}; $mgkg^{-1}$)	0.16±0.01	0.17±0.04	0.14±0.01	0.14±0.01	11.90±0.78	17.45±3.33	14.75±1.02	8.52±4.12	0.398	0.602
Na^+ (mgL^{-1}; $mgkg^{-1}$)	0.13±0.02	0.42±0.28	0.16±0.03	0.17±0.02	0.08±0.03	0.09±0.00	0.10±0.00	0.10±0.00	0.979	0.021
K^+ (mgL^{-1}; $mgkg^{-1}$)	0.80±0.21	1.25±0.91	1.52±0.56	2.09±0.77	0.47±0.20	0.67±0.00	0.43±0.00	1.14±0.00	0.217	0.783
U-238 ($Bqkg^{-1}$; BqL^{-1})	2.23±0.15	1.24±0.15	1.06±0.20	1.09±0.25	34.78±14.80	32.05±7.50	34.04±5.50	41.27±6.00	0.799	0.201
Th-232 ($Bqkg^{-1}$; BqL^{-1})	1.08±0.24	0.74±0.11	0.32±0.09	0.20±0.09	67.46±9.55	79.45±19.00	55.67±11.50	84.07±13.00	0.908	0.092
K-40 ($Bqkg^{-1}$; BqL^{-1})	9.49±0.90	7.23±0.45	4.74±0.15	4.04±0.10	650.21±89.67	236.30±3.00	384.01±3.00	503.20±6.50	0.676	0.324

NB: Using sig 0.01 and 0.05 (99% and 95% confidence), significance values below 0.01 are very significant, significance values below 0.05 are significant, significance values above 0.05 are not significant.

among the radionuclides in both water and sediment. Also, K^+ has the highest concentration among the cations in both water and sediment. This observation agrees with Ugbede et al. (2020) and it could be because Potassium-40 is a natural radionuclide that abounds in the earth crust and its high concentration in the stream may be due to leaching of topsoil of the farmlands that makes use of inorganic potassium fertilizers to enhance soil nutrients. According to Omale et al. (2014), elements with high affinity for organic or inorganic particles in the water will typically be concentrated in the sediment from which they can in turn be remobilized and re-suspended in the water column. Therefore, the findings of this study could be because high organic materials are presents in the sampling sites, and the radionuclides are typically concentrated more in the sediments than in water throughout the year. This study agrees with Omale et al. (2014) and Orosun et al. (2021) that higher concentrations of radioactive elements are often found in soils and sediments than in water.

However, parameters such as Mg^{2+}, NO_3^-, Na^+, and K-40 show strong correlation between water and sediment samples in wet season while SO_4^{2-}, Mg^{2+}, NO_3^-, and K^+ show strong correlation between water and sediment in dry season (Table 7 and 8).

Overall, the mean annual effective dose (AED) per person for all the radionuclides in all sampling locations are all below the NIS limit and the WHO recommended level of 0.1 $mSvy^{-1}$ for drinking water and also below the tolerable level of 1 $mSvy^{-1}$ to the general public for prolonged exposure as recommended by the International Commission on Radiological Protection (ICRP, 2000; WHO, 2006) (Table 4).

Conclusion

This study concluded that Uranium-238, Potassium-40, and Thorium-232 have their highest mean AC in ground water. However, the mean AC of U-238, Th-232 and K-40 in surface water were higher in the wet season than in the dry season. Furthermore, the mean annual effective dose (AED) per person for all the radionuclides and the ions are all below the NIS limit and the WHO recommended level of 0.1$mSvy^{-1}$ for drinking water and also below the tolerable level of 1$mSvy^{-1}$to the general public for prolonged exposure as recommended by the International Commission on Radiological Protection. It also documented that cations in sediment samples were observed to be high in dry season compared to wet season. However, the concentration of radionuclides and most ions in this study were discovered to be significantly low in sediment during wet season than in dry season. The mean concentration values of Cl^-, Na^+, Mg^{2+}, Ca^{2+}, and K^+ are higher in water than in sediment while the mean concentration values of SO_4^{2-}, NO_3^-, U-238, Th-232 and K-40 are all higher in sediment. Also, K^+ has the highest concentration among the cations in both water and sediment. It will be of immense benefit to the public if constant monitoring of radionuclides and other environmental parameters in the study area should be carried out to determine the cumulative concentration of these radionuclides in water and sediment with time.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

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