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Determination of radionuclides and elemental composition of clay soils by gamma- and X-ray spectrometry

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Abstract

Radiochemical and elemental analysis of clay soils collected from different locations within Ekiti State have been performed in this study using gamma and XRF spectrometric measurements. The results of this study show that the mean concentrations of uranium ranged from 2.2 ± 1.0 mg/kg to 3.2 ± 1.1 mg/kg, that of thorium ranged from 4.0 ± 0.5 mg/kg to 5.7 ± 1.7 mg/kg, while potassium presented in % by weight ranged from 0.4 ± 0.2 to 1.3 ± 0.3 in all the locations. The overall mean concentrations of these radionuclides are comparable to values from other locations around the world. The XRF analysis revealed 4 major elements and 11 minor or trace elements present in the clay samples. The distribution of the various major and trace elements in all the sampling sites do not follow any systematic trend but vary from point to point. To assess the level of contamination and the possible anthropogenic impact in the clay soils, the enrichment factor (EF) and the geoaccumulation index (Igeo) were estimated for some potential hazardous elements. The results indicate that Cu, Zn, Ni and Mn have $EF < 2$ indicating minimal or no enrichment while Pb is moderately enriched in all the locations.

Keywords: Gamma spectrometry, XRF, Clay soil, Enrichment factor, Geoaccumulation index

Background

The earth crust contains small amount of uranium, thorium, potassium and other trace and major elements such as Cs, Cd, Pb, Fe, Mg, Mn, etc. The concentrations of all these elements depend on the geology of a local environment as well as other natural and anthropogenic processes. The average concentration of uranium in the earth crust has been reported to be in the range of 2–3 ppm, while thorium exists in the range of 8–12 ppm (IAEA, 2003a). Potassium is widely distributed in nature, with concentrations varying from about 0.1% for limestone, through 1% for sandstones to as much as 3.5% for some granite (Eisenbud, 1987; Eisenbud and Gesell, 1997). The concentrations of major and trace elements in environmental samples had been studied by several authors using either atomic absorption spectrometry (AAS) (Mico et al., 2006; Fagbote and Olanipekun, 2010; Zheng et al., 2010; Ghrefat et al., 2010; Ali and Malik, 2011) or XRF analysis (Kierzek et al., 1999; Boyle, 2000; Baranowski et al., 2002;

Zhang et al., 2003; Rauf et al., 2004; Bakraji et al., 2010). Most of these studies indicate high concentrations of major and minor elements in the environment. Pollution of natural environment by metals is a worldwide problem because these metals are indestructible and many of them have toxic effects on living organism, especially when they exceed certain threshold (Forstner, 1990; Ghrefat and Yusuf, 2006).

Soil forms a major component of an ecosystem and is the most endangered due to the influence of various human activities such as urban development, industrial and technological advancements, agricultural practices and indiscriminate waste disposal. Soil is considered contaminated when chemicals are present or other alterations have been made to its natural environment (Gowd et al., 2010). Clay is a natural earthy fine grained inorganic material that develops plasticity when mixed with limited amount of water (McGraw-Hill, 1997; Odo et al. 2008). Its origin could be traced to the breaking down of granite rocks by physical and chemical processes called weathering. Natural clay minerals are well known to mankind from the earliest days of

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civilization and because of their low cost, abundance in most continents of the world, high sorption characteristics and potential for ion exchange, they form a good material for absorbents (Nayak and Singh, 2007). Clay soils generally contain mostly silica (47%) and alumina (40%), elemental analysis have shown that a great number of minor and trace metallic elements such as Sc, Cr, Cu, Ti, Ga, Zr, Mn, Mg, Sr and Pb exist in clay soil. There are several classes of clay which include; smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite (Nayak and Singh, 2007). The specific elemental composition of each clay material will usually depend on the amount of the element present in the host rock, the chemical association of the elements with stable and/or unstable mineral during weathering and the intensity of drainage and other polygenetic alterations associated with clay materials (Ibeanu et al., 1997). It has a wide range of applications in the building and ceramic industries. In the rural area, clay is used for the building of earthen or mud houses, while in the urban area, it is used for making burnt bricks used in building modern dwellings. Clay has been in use for making pottery in different continents of the world for several centuries. It is also used in the manufacturing of refractory's products and serves as a natural filter for underground water. In some continents of the world, including Africa, it is a common practice for people to engage in the act of eating clay (geophagia) during pregnancy or for curative purposes. All these may lead to direct or indirect accumulation of metals in man.

XRF is a rapid, non-destructive multi-elemental analysis technique with sensitivity in the range of 10^{-8} (IAEA, 2003b) and it is ideal for environmental research. This analytical method has been widely and routinely applied to the analysis of various archaeological samples, historical relics and works of art (Bakraji et al., 2010; Pillay, 2001; Feretti, 2000). XRF can analyze some 15–30 elements with atomic numbers ranging from $Z = 11$ to $Z = 41$ and some rare earth elements (REEs) (Bakraji et al., 2010). X-ray fluorescence (XRF) analysis is based on the measurement of characteristic X-rays resulting from de-excitation of inner shell vacancy produced in a sample by means of a suitable source of radiation. Energy-dispersive XRF analysis (EDXRF) employs detectors that directly measure the energy of the X-rays by collecting the ionization products in a suitable detecting medium (Tajani and Markowicz, 2004). Gamma ray spectrometry is another analytical technique used widely in environmental investigations. It is used mainly for the determination of the concentrations of radioactive elements that decay through gamma emission. The use of gamma ray spectrometry as a tool for mapping radioelemental concentrations has found widespread acceptance in diverse fields. The method is

widely used for environmental monitoring, geological mapping and mineral exploration. It is also a non-radioanalytical technique. Even though, there are many naturally occurring elements that have radioactive isotopes, only potassium and the uranium and thorium decay series, have radioisotopes that produce gamma rays of sufficient energy and intensity measurable by gamma ray spectrometry due to their relative abundance in nature. Geochemical analysis of the total concentrations of major rock-forming elements is important because they provide valuable information about the geochemical properties of the soil in any given environment. The crossed analysis of geochemical and radiometric data provides a useful tool for a better understanding of the origin and characteristics of different rocks (Brai et al. 2006) and soils. It is reported in literature that higher percentage of some metallic oxides in rocks and soil will result in higher specific activities of primordial radionuclides such as ^{238}U , ^{232}Th and ^{40}K in such rocks and soil (Brai et al. 2006). The present work is aimed at evaluating the radionuclides and elemental composition of clay soil using gamma- and X-ray spectrometry. It is also the objective of the study to assess the extent and degree of pollution by metals and identify the origin of the metals using the enrichment factor and geo-accumulation index.

Materials and methods

Sample collection

The clay samples used for these analyses were collected from five major clay deposits identified within Ekiti State in the south-western part of Nigeria. The study area is situated between longitudes $4^{\circ} 45''$ to $5^{\circ} 45''$ East of the Greenwich Meridian and latitudes $7^{\circ} 15''$ to $8^{\circ} 5''$ North of the Equator. The area is completely within the geological basement complex region of Nigeria. In all, 25 samples were analyzed for their radionuclides and elemental concentrations. The samples were collected directly from the existing mining sites. This gives a good representation of the actual material being utilized either as building material or those used in pottery making. The collected samples were packed into black polythene bags and transported to the laboratory where they were initially air dried at room temperature for about 5 days in order to reduce the moisture content.

Sample preparation and measurement for XRF analysis

To satisfy homogeneity condition of XRF analysis, the clay samples were pulverized manually to very fine powder with an agate mortar and pestle. Pellets of 13 mm diameter were made from 0.3–0.4 g powder without binder at 8 tons of pressure with a hydraulic press. The pellets were kept in different polythene bags which were in turn kept in polypropylene container until analysis. Each sample pellet was irradiated for 1000 seconds at

fixed condition of 25 kV and 50 μ A. The elemental analysis of the samples was performed using the Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The EDXRF spectrometer consists of a self-contained miniature X-ray tube system ECLIPSE-III, which includes the X-ray tube with a silver (Ag) transmission target, and a beryllium window, a portable Controller incorporating the power supply and control electronics. The Controller generates all the voltages needed to operate the x-ray tube and provides both voltage (kV) and current (μ A) display and control. The X-Ray Detector is a Model XR-100CR, high performance thermoelectrically cooled Si-PIN photodiode, with a preamplifier. The detector is powered by the PX2 CR Power supply, which includes a spectroscopy grade Shaping Amplifier. The detector system has a resolution of 220 eV FWHM, for the 5.9 keV peak of ^{55}Fe . The detector is coupled to MCA8000A Multichannel Analyzer for signal processing and data acquisition. The spectrum of Orin sample #5 is shown in Figure 1, while the Logarithm Scale of the same sample is shown in Figure 2. The X-ray tube, ECLIPSE-III with associated Controller/power supply, the Detector system and the Multichannel Analyzer were all supplied by AMPTEK INC., MA USA. The quantitative analysis of the samples was carried out using Fundamental Parameter (FP)

method with XRF-FP Software package by CrossRoad Scientific.

Sample preparation and measurement for Gamma ray spectrometric analysis

Detailed procedure for the preparation and measurement of gamma emitting radionuclides in the clay samples is reported elsewhere (Isinkaye and Shitta, 2010). The air-dried samples were pulverized into powder to achieve uniform matrix similar to the standard sample. All the samples were stored for an upward of 40 d in radon impermeable plastic containers prior to analysis. A 7.6 cm \times 7.6 cm NaI(Tl) detector optically coupled to photomultiplier tube was used for the measurement of gamma emitting radionuclides in the clay samples. A multi-channel analyzer matched to an IBM- Compatible personal computer was used for the pulse processing and data analysis. The spectrometer was calibrated against reference material with known activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K (Isinkaye and Shitta, 2010). The detector has a resolution of 8% at the 0.662 MeV line of ^{137}Cs , which is capable of distinguishing the gamma-ray energies of the radionuclides considered in this study. The activity concentrations of ^{226}Ra and ^{232}Th were determined from the gamma lines associated with their respective short-lived daughters; ^{214}Bi (1760 keV) and ^{208}Tl (2615 keV). Each of the samples and the background was counted for

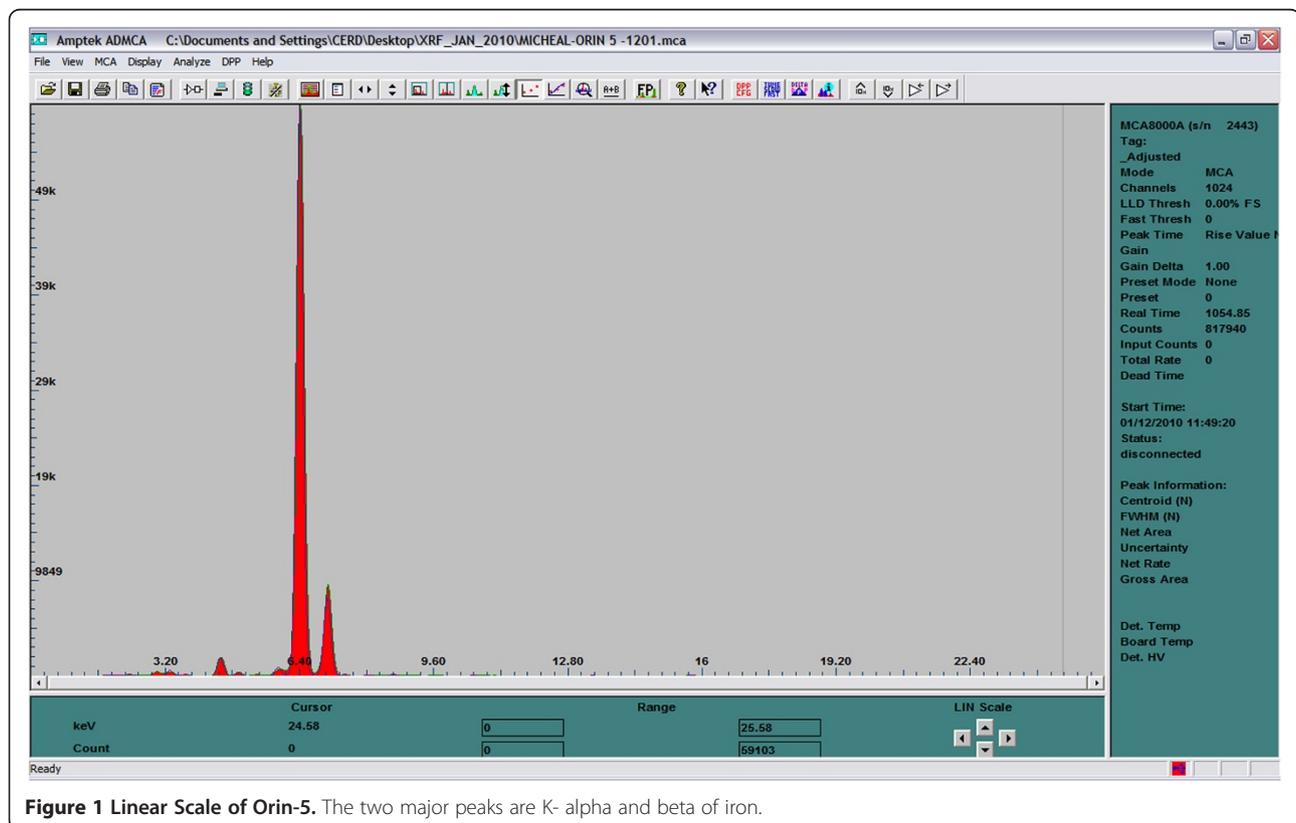


Figure 1 Linear Scale of Orin-5. The two major peaks are K- alpha and beta of iron.

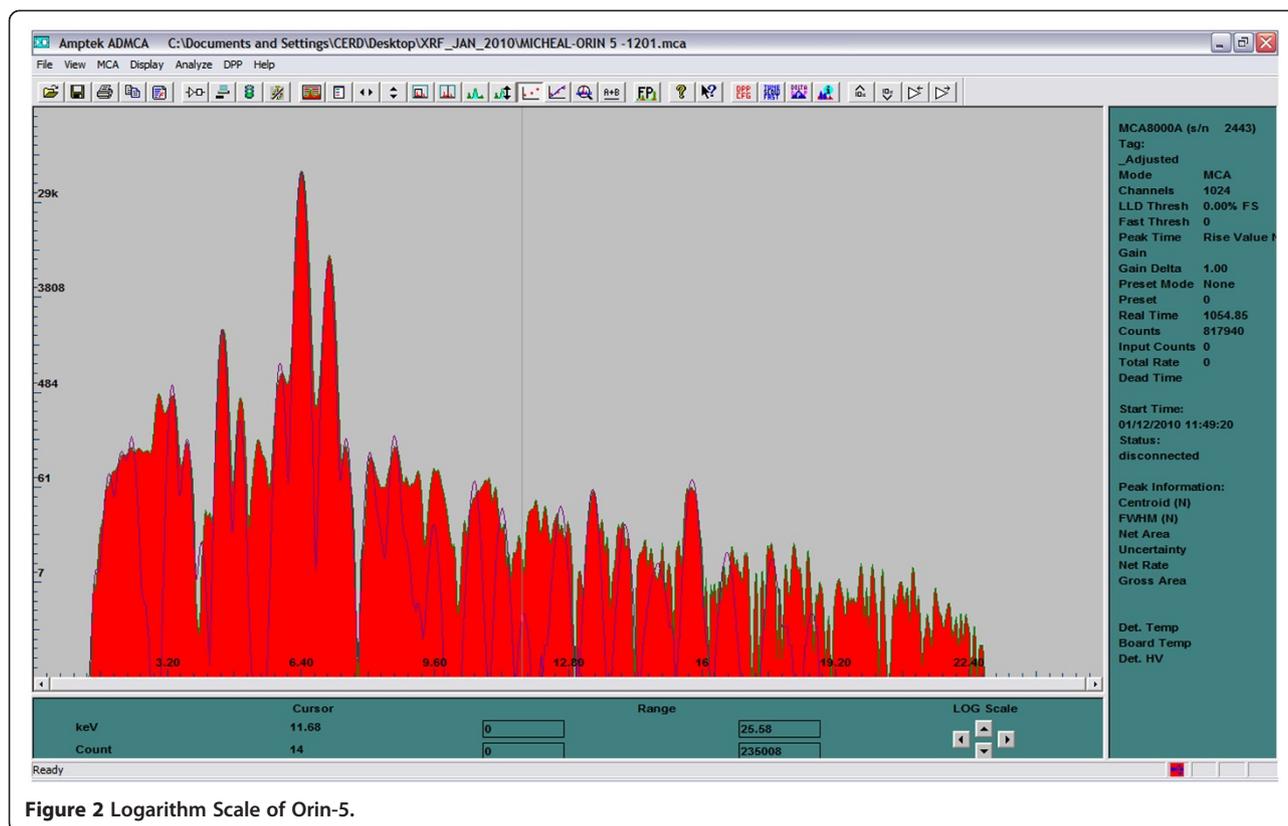


Figure 2 Logarithm Scale of Orin-5.

10 h. The background spectral was deducted from the gross count to obtain the net count due to the sample alone.

Evaluation of massic elemental concentrations

The activity concentrations of ^{238}U , ^{232}Th and ^{40}K in Bqkg^{-1} were converted into massic elemental concentrations in part per million (ppm) units for uranium and thorium, and % by weight for potassium, respectively, according to the following equation (Dragovic et al., 2006):

$$F_E = \frac{M_E C}{\lambda_{E,i} N_A f_{E,i}} A_{E,i} \quad (1)$$

where F_E is the fraction of element E in the sample, M_E is the atomic mass (kg mol^{-1}), $\lambda_{E,i}$ is the decay constant of the measured isotope of element E (s^{-1}), $f_{E,i}$ is the fractional atomic abundance in nature, and $A_{E,i}$ is the measured specific activity (Bq kg^{-1}) of the radionuclide under consideration (^{238}U , ^{232}Th and ^{40}K), N_A is the Avogadro's number (6.023×10^{23} atoms mol^{-1}), and C is a constant with value of 1,000,000 for U and Th (concentration in ppm) or 100 for K (concentration in % of mass fraction).

Results and discussion

The concentrations of 15 major and minor elements together with three radionuclides are presented in Tables 1, 2 and 3. The major elements, Fe, Ti, Ca, and K were estimated as their respective oxides and are given in % by weight, while the minor elements, Cu, Zn, Mn, Zr, Ni, Se, Rb, Sr, Nb, Pb and As are presented in mg/kg unit. The naturally occurring radionuclides; U and Th are presented in ppm units while K is presented in % by weight. The discussion on each group is presented below:

Naturally occurring radionuclides

The massic elemental concentrations of three naturally occurring radionuclides U, Th and K measured in the clay soil samples investigated in this study are presented in Table 1. Ado Ekiti samples have the highest mean concentration of uranium and potassium, and the highest mean concentration of thorium is found in Orin Ekiti. All the lowest mean concentrations are obtained in Isan Ekiti. The concentrations of the three radionuclides, U, Th and K, ranged from 1.2–4.1 ppm, 2.7–8.2 ppm and 0.1–1.6%, respectively. These radionuclides showed a range of concentrations, as a consequence of varying geological composition of the studied area.

Massic concentrations of U, Th and K in comparison with other locations around the world is presented

Table 1 Mass concentrations of U, Th and K and external gamma dose rate in clay soil samples

Element	Ado Ekiti Range (Mean ± SD)	Ara-Ijero Ekiti Range (Mean ± SD)	Ire Ekiti Range (Mean ± SD)	Isan Ekiti Range (Mean ± SD)	Orin Ekiti Range (Mean ± SD)
U (ppm)	1.6-4.0 (3.2 ± 1.1)	2.0-3.6 (2.6 ± 0.7)	1.6-4.1 (3.1 ± 1.2)	1.2-3.4 (2.2 ± 1.0)	1.5-3.2 (2.5 ± 0.8)
²³² Th (ppm)	3.3-7.2 (5.3 ± 1.6)	4.2-6.5 (5.6 ± 1.0)	2.7-6.4 (4.2 ± 1.4)	3.3-4.5 (4.0 ± 0.5)	3.7-8.2 (5.7 ± 1.7)
K (%)	1.0-1.6 (1.3 ± 0.3)	0.1-0.7 (0.4 ± 0.3)	0.2-0.9 (0.5 ± 0.3)	0.2-0.8 (0.4 ± 0.2)	0.3-1.2 (0.7 ± 0.3)
Dose rate (nGyh ⁻¹)	30.0-62.3 (48.1 ± 12.2)	26.6-39.5 (34.6 ± 10.2)	(22.5-43.7) 34.8 ± 6.2	(20.6-40.7) 27.2 ± 8.4	(21.8-49.9) 37.5 ± 11.3

in Table 4. The mean U (ppm) concentration obtained in this study is greater than values obtained in Albania, Australia, Cyprus and Italy, lower than values obtained in Canada, Egypt and Jordan but comparable to values obtained in Serbia and Montenegro, and USA (Table 4). The mean concentration of Th (ppm) is higher than those obtained in Cyprus and Egypt but lower than those obtained in Albania, Australia, Bulgaria, Canada, Italy, Jordan, Serbia and Montenegro, and USA. The mean concentration of K (%) is however lower than the values obtained in all these country except Cyprus. All the radionuclides concentrations except uranium are lower than the world average values (Table 4).

Estimation of gamma dose rate

The radiological implications of the activity concentrations of the naturally occurring radionuclides present in the clay samples were estimated using the external gamma dose rates at 1 m above an infinite homogeneous soil medium per unit radioelement concentration assuming radioactive equilibrium in the uranium and thorium decay series. In the calculation, the contributions of artificial radionuclides such as ¹³⁷Cs and ⁹⁰Sr were neglected. The calculations

were performed according to the following equation (IAEA, 2003a; Lovborg, 1984):

$$D = [13.078A_K + 5.675A_U + 2.494A_{Th}]nGyh^{-1} \quad (2)$$

Where, A_K is the mass concentration of K in %, A_U is the mass concentration of uranium in ppm and A_{Th} is the mass concentration of thorium in ppm. The estimation is based on the assumption that 1%K corresponds to 13.078 nGyh⁻¹, 1 ppmU gives 5.675 nGyh⁻¹ and 1 ppmTh is equivalent to 2.494 nGyh⁻¹dose rate, respectively. The range and mean dose rates obtained for all the clay samples in the study locations are presented in Table 1. All the mean gamma dose rates obtained for the five study locations are lower than the world average value of 59 nGyh⁻¹ (UNSCEAR, 2000). The effective dose was also estimated using the formula suggested by Dragovic et al., (2006):

$$H_E = [D \times 24 \times 365 \times 0.7 \times 0.2] \quad (3)$$

Where D is the gamma dose rate obtained from mass concentrations of U, Th and K, 0.7 SvGy⁻¹ is the conversion coefficient from absorbed dose in air to effective dose and 0.2 represents the outdoor occupancy factor,

Table 2 Concentrations of major elements in clay soil samples

Element	Ado Ekiti Range (Mean ± SD)	Ara-Ijero Ekiti Range (Mean ± SD)	Ire Ekiti Range (Mean ± SD)	Isan Ekiti Range (Mean ± SD)	Orin Ekiti Range (Mean ± SD)
No of Sample	5	5	5	5	5
Fe ₂ O ₃ (%)	1.9-17.4 (10.5 ± 7.7)	4.9-14.4 (11.1 ± 3.9)	3.5-16.4 (9.7 ± 5.2)	6.0-22.3 (16.2 ± 6.2)	2.8-12.7 (7.9 ± 3.9)
TiO ₂ (%)	1.2-4.7 (3.2 ± 1.7)	3.6-5.7 (4.9 ± 0.9)	0.8-4.2 (2.8 ± 1.2)	6.2-10.4 (7.6 ± 1.6)	1.3-4.2 (2.9 ± 1.4)
CaO (%)	0.9-6.5 (3.9 ± 2.4)	1.0-3.5 (2.3 ± 1.0)	0.2-2.5 (1.2 ± 0.9)	2.3-4.7 (3.3 ± 0.9)	0.2-5.0 (1.6 ± 1.3)
K ₂ O (%)	1.2-9.9 (3.2 ± 1.7)	3.8-9.2 (5.8 ± 2.0)	0.6-5.8 (2.8 ± 2.0)	5.3-9.0 (6.3 ± 1.5)	0.7-9.5 (4.4 ± 3.3)

Table 3 Concentrations of minor or trace elements in clay soil samples

Element	Ado Ekiti Range (Mean ± SD)	Ara-Ijero Ekiti Range (Mean ± SD)	Ire Ekiti Range (Mean ± SD)	Isan Ekiti Range (Mean ± SD)	Orin Ekiti Range (Mean ± SD)
Cu (ppm)	32-165 (100.6 ± 61.6)	28-190 (107.6 ± 63.1)	22-176 (91.6 ± 60.8)	18-195 143.2 ± 71.9	17-174 (82.6 ± 60.9)
Zn (ppm)	90-246 (161.0 ± 71.9)	88-290 (184.2 ± 76.0)	74-364 (202.4 ± 124.3)	95-311 257.2 ± 92.5	67-246 (166.4 ± 84.7)
Mn (ppm)	219-2823 (1593.0 ± 1190.4)	605-2539 (1869.4 ± 785.2)	452-3606 (1682.8 ± 1306.7)	780-5296 3780.6 ± 1870.7	710-2000 (1451.4 ± 596.8)
Zr (ppm)	151-953 (443.2 ± 314.5)	166-813 (389.0 ± 252.4)	46-270 150.2 ± 95.0	222-486 332.4 ± 95.7	105-1439 (439.0 ± 56.4)
Ni (ppm)	88-194 (136.8 ± 43.5)	32-269 (151.8 ± 95.0)	33-336 180.4 ± 128.0	27-216 133.2 ± 69.5	22-273 (147.2 ± 93.5)
Se (ppm)	23-68 (49.0 ± 18.9)	49-97 (65.5 ± 21.0)	44-61 54.8 ± 8.1	43-98 69.5 ± 23.3	42-101 (63.3 ± 25.9)
Rb (ppm)	33-104 (63.0 ± 31.6)	171-234 (202.8 ± 30.4)	30-234 107.0 ± 90.4	169-282 225.5 ± 50.2	21-188 (117.0 ± 74.2)
Sr (ppm)	13-89 (57.8 ± 31.9)	91-118 (106.8 ± 12.0)	10-90 36.6 ± 31.7	121-346 225.0 ± 80.4	23-256 (91.0 ± 38.8)
Nb (ppm)	35-120 (78.3 ± 41.5)	34-94 (76.3 ± 28.2)	28-99 63.8 ± 29.1	54-114 90.5 ± 28.0	24-79 (51.8 ± 26.8)
Pb (ppm)	73-499 (232.2 ± 164.5)	75-310 (199.8 ± 100.9)	72-311 174.4 ± 118.0	86-317 247.2	70-232 (150.6 ± 76.6)
As (ppm)	137-183 (160.0 ± 32.5)	ND	ND	ND-49 23.0 ± 22.7	ND

Table 4 The comparison of the mass concentrations of U, Th and K in clay soil samples of the present study with other locations around the world

Location	U (ppm)	Th (ppm)	K (%)	Reference
Albania*	0.48-7.68 (1.84)	0.98-39.5 (5.93)	0.05-3.75 (1.17)	UNSCEAR (2000)
Australia	Rock 2.1-3.6 (2.5)	18-55 (15)	2.4-3.8 (2.4)	Dickson and Scott (1997)
	Soil 1.6-3.8 (2.2)	6-19 (1.3)	0.7-1.9 (1.3)	
Bulgaria*	0.64-15.2 (3.2)	1.73-39.5 (7.41)	0.05-3.75 (1.17)	UNSCEAR (2000)
Canada (Rock)	0.8-16.4 (4.1)	1.1-41.0 (11.9)	1.0-6.2 (3.1)	Killeen (1979)
Cyprus*	0.08-7.2 (1.2)	0.25-13.1 (2.72)	0.04-2.91 (0.58)	Tzortzi et al. (2003)
Italy*	0.16-5.6	0.25-16.8 (5.43)	0.03-5.14 (1.41)	Chiozzi et al. (2002)
Egypt*	0.48-9.6 (2.96)	0.49-23.7 (4.45)	0.09-2.12 (1.04)	UNSCEAR (2000)
Jordan*	1.76-8.32 (6.72)	5.18-25.4 (20.2)	0.45-1.96 (1.82)	Al-Jundi et al. (2003)
Serbia and Montenegro	1.2-6.24 (2.76)	4.45-21.0 (10.4)	0.88-2.99 (1.98)	Dragovic et al. (2006)
USA*	0.32-11.2	0.98-32.1 (8.20)	0.32-2.28 (1.21)	Myrick et al. (1983)
World Average	2.64	11.1	1.37	Dragovic et al. (2006)
Present study	1.2-4.1 (2.7)	2.7-8.2 (4.9)	0.1-1.63 (0.7)	

* Sourced from Dragovic et al. (2006).

Table 5 Average concentrations of selected elements, average shale (ppm) (Turekian and Wedepohl, 1961), enrichment factor and the geoaccumulation index values in the clay samples

Elements	Average Shale Value	Ado Ekiti	EF	I_{geo}	Ara-Ijero Ekiti	EF	I_{geo}	Ire Ekiti	EF	I_{geo}	Isan Ekiti	EF	I_{geo}	Orin Ekiti	EF	I_{geo}
Cu	45	100.6	1.00	0.58	107.6	1.01	0.67	91.6	0.99	0.44	143.2	0.92	1.09	82.6	1.09	0.29
Zn	95	161	0.76	0.18	184.2	0.82	0.37	202.4	1.03	0.51	257.2	0.79	0.85	166.4	1.04	0.22
Ni	68	136.8	0.90	0.42	151.8	0.95	0.57	180.4	1.29	0.82	133.2	0.57	0.39	147.2	1.29	0.53
Mn	850	1593	0.84	0.32	1869.4	0.93	0.55	1682.8	0.96	0.40	3780.6	1.29	1.57	1451.4	1.02	0.19
Pb	20	232.2	5.20	2.95	199.8	4.23	2.74	174.4	4.23	2.54	247.2	3.59	3.04	150.6	4.48	2.33
As	13	160	5.51	3.04	-	-	-	-	-	-	23	0.51	-	-	-	-

which shows that the people in the study area spend ~20% of their time outdoor. The mean annual effective dose obtained in the study area varied from 0.03–0.06 mSv., which fall below the worldwide mean annual effective dose value of 0.07 mSv. The results obtained indicate that the study area can be categorized as area with normal background radiation.

Major elements

The lowest mean concentration value ($7.9 \pm 3.9\%$) of Fe_2O_3 obtained in this study is found in Orin-Ekiti while the highest mean concentration value of $16.2 \pm 6.2\%$ is obtained in Isan-Ekiti. The values obtained in all sampling points ranged from 1.9–22.3%. The mean concentrations of Fe_2O_3 in all the five locations are higher than the average crustal value reported in Turekian and Wedepohl (1961). The values are also higher than mean value obtained in a Mediterranean agricultural soil in Spain. The high concentration of Fe in the clay soils is generally not of any major concern because Fe is not a contaminant element. Fe is important in plant nutrition and an essential crop micronutrient. The mean concentrations of TiO_2 follow the same trend as Fe_2O_3 with lowest mean value ($2.9 \pm 1.4\%$) obtained in Orin-Ekiti while the highest mean value of $7.9 \pm 1.6\%$ is obtained in Isan-Ekiti. TiO_2 is the most common compound of Titanium and is widely distributed in the Earth’s crust. It is found in almost all

living things, rocks, water bodies and soil (Wikipedia, 2011). Its proportion in soil is approximately 0.5–1.5% (Barksdale, 1968). The concentration of CaO varied from 0.2–6.5% with highest mean concentration found in Ado-Ekiti and the lowest concentration obtained in Ire-Ekiti. Similarly, the concentrations of K_2O vary from 0.6–9.9% with highest and lowest mean concentrations of $6.3 \pm 1.5\%$ and $2.8 \pm 2.0\%$ respectively. The Ca and K concentrations obtained in this study are comparable to the values obtained by XRF analysis of some clay samples in Pakistan (Baranowski et al., 2002). Their results indicate a range of Ca to be 0.10–8.9% while K ranged from 0.05–2.25%. Also the levels of Ca and K obtained in this study is higher than mean concentrations of 0.35% and 0.24% obtained respectively for Ca and K in coal samples by Kierzek et al. (1999).

Minor elements

The results showed that Mn has the highest overall mean concentration, followed by Zr, Pb, Zn, Sr, Nb, Se, As (Table 3). All the sampling locations showed higher Cu, Zn, Mn, Ni, Pb and As contents than the values obtained for average shale as reported by Turekian and Wedepohl (1961). As seen, the distributions of these minor elements vary much from different sampling locations i.e the distribution does not follow any systematic trend. For Cu, the

Table 6 Geoaccumulation index (I_{geo}) for contamination levels in clay soil samples

I_{geo} class	I_{geo} value	Contamination level
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} \leq 1$	Uncontaminated/moderately contaminated
2	$1 < I_{geo} \leq 2$	Moderately contaminated
3	$2 < I_{geo} \leq 3$	Moderately/strongly contaminated
4	$3 < I_{geo} \leq 4$	Strongly contaminated
5	$4 < I_{geo} \leq 5$	Strongly/extremely contaminated
6	$I_{geo} > 5$	Extremely contaminated

Table 7 Descriptive statistics of massic elemental concentrations of U, Th and K for all the analyzed clay samples

Parameter	Massic elemental concentration		
	U (ppm)	Th (ppm)	K (%)
Mean	2.7212	4.9229	0.6716
Standard deviation	0.96973	1.40750	0.42847
Maximum	4.11	8.20	1.63
Minimum	1.17	2.73	0.09
Median	2.6215	4.5394	0.6670
Skewness	-0.005	0.564	0.518
Kurtosis	-1.366	-0.384	-0.596

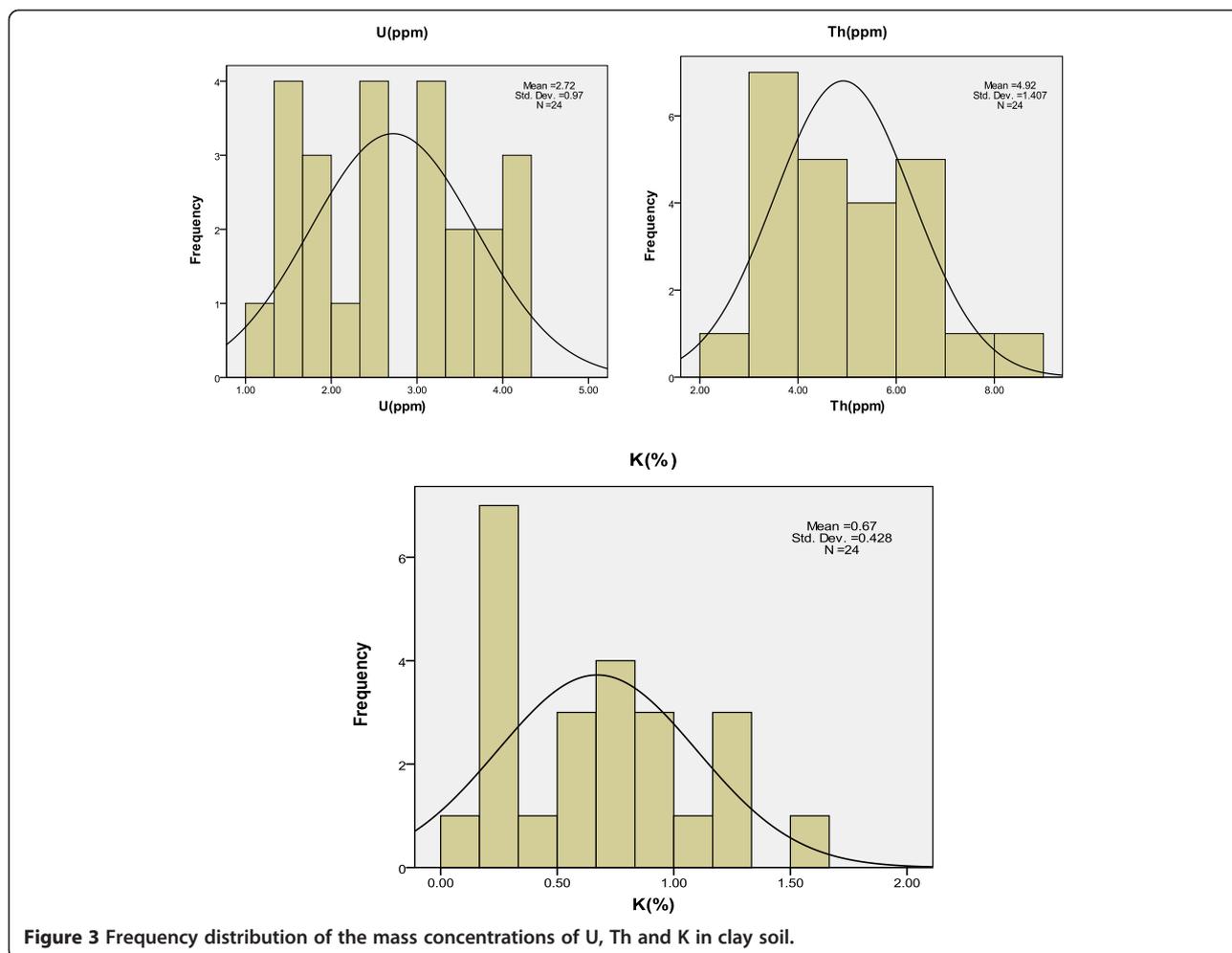


Figure 3 Frequency distribution of the mass concentrations of U, Th and K in clay soil.

mean concentrations vary from 82.6 ± 60.9 - 143.2 ± 71.9 mg/kg, Zn, 166.4 ± 84.7 - 257.2 ± 92.5 mg/kg, Mn, 1451.4 ± 596.8 - 3780.6 ± 1870.7 mg/kg, Zr, 150.2 ± 95.0 - 443.2 ± 314.5 mg/kg, Ni, 133.2 ± 69.5 - 180.4 ± 128.0 mg/kg, Se, 49.0 ± 18.9 - 69.5 ± 23.3 mg/kg, Rb, 63.0 ± 31.6 - 225.5 ± 50.2 mg/kg, Sr, 36.6 ± 31.7 - 225.0 ± 80.4 mg/kg, Nb, 51.8 ± 26.8 - 90.5 ± 28.0 mg/kg, Pb, 150.6 ± 76.6 - $247.2 \pm$ mg/kg, and As, 23.0 ± 22.7 - 160.0 ± 32.5 mg/kg. The high standard deviation values indicate the spread in the distribution of the minor elements in all the sampling sites. Most of the minor elements have their highest mean concentrations at Isan-Ekiti sampling sites. Isan-Ekiti clay is kaolinic in nature and it is used extensively in making earthen vessels used by local populace for cooking. This could pose metal poisoning and some other detrimental health hazard. Some of the potentially hazardous element such as Cu, Zn, Ni, Pb and As have their mean concentrations higher than the maximum allowable concentration values in clay soil as applied in the Federal Republic of Germany. For Cu, Zn, Ni and Pb, the maximum allowable concentration in clay soil are respectively, 60 mg/kg, 200 mg/kg, 70 mg/kg and 100 mg/kg.

Enrichment factor and geoaccumulation index

In order to assess the level of contamination and the possible anthropogenic impact in the clay samples, the enrichment factors (EF) and geoaccumulation index (I_{geo}) were estimated for some selected potentially hazardous elements evaluated in this study. The enrichment factor is defined as:

$$EF = \frac{\left(\frac{C_x}{C_{Fe}}\right)_{sample}}{\left(\frac{C_x}{C_{Fe}}\right)_{reference}} \quad (4)$$

Where C_x is the concentration of the potentially enrichment element and C_{Fe} is the concentration of the proxy or normalizing element usually Fe. The world average elemental concentrations reported by Turekian and Wedepohl (1961) in the earth's crust were used as reference in this study because regional geochemical background values for these elements are not available. Five major contamination categories are recognize on the basis of the enrichment factor, where, $EF < 2$ is deficient to minimal enrichment, $2 \leq EF < 5$ is moderate enrichment, $5 \leq EF < 20$ is significant enrichment, $20 \leq EF <$

Table 8 Pearson correlation coefficients between natural radionuclides and elemental concentrations in clay soil samples

Variable	K(%)	U(ppm)	Th(ppm)	Fe	Ti	Ca	K	Cu	Zn	Mn	Zr	Ni	Se	Rb	Sr	Nb	Pb	As
K(%)	1																	
U(ppm)	.499*	1																
Th(ppm)	.299	.426*	1															
Fe	-.022	.079	.161	1														
Ti	-.292	-.296	.001	.574**	1													
Ca	.170	-.194	-.019	.406*	.215	1												
K	-.472*	-.366	.103	.157	.244	.486*	1											
Cu	-.020	.030	.173	.910**	.592**	.229	-.007	1										
Zn	-.165	-.075	.105	.864**	.499*	.113	.001	.906**	1									
Mn	-.176	-.071	.014	.913**	.577**	.272	.184	.866**	.858**	1								
Zr	-.100	-.085	.015	-.198	-.096	.406*	.389	-.263	-.292	-.139	1							
Ni	-.056	.074	.291	.550**	.239	-.172	-.264	.762**	.775**	.501*	-.369	1						
Se	.121	.186	.342	.590**	.153	-.140	-.116	.639**	.651**	.616**	-.496*	.534**	1					
Rb	-.252	-.113	.084	.765**	.446*	-.016	.104	.758**	.823**	.796**	-.305	.546**	.753**	1				
Sr	-.446*	-.452*	-.194	.216	.454*	.503*	.695**	.062	.077	.317	.417*	-.258	-.149	.165	1			
Nb	.065	.059	.139	.806**	.328	.204	-.192	.835**	.827**	.779**	-.297	.677**	.671**	.717**	-.104	1		
Pb	.161	.248	.383	.839**	.397*	.333	-.049	.843**	.783**	.741**	-.149	.678**	.622**	.600**	.031	.816**	1	
As	.570**	.224	.147	.414*	.067	.591**	-.310	.343	.215	.223	.075	.145	.062	-.016	-.099	.430*	.564**	1

*Significant at the 0.05 level.
 ** Significant at the 0.01 level.

40 means high enrichment, and $EF > 40$ indicates extremely high enrichment. EF can easily be used to differentiate between elemental concentrations from anthropogenic source and those from natural origin. According to Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate the metal is entirely from crustal materials or natural origin, while $EF > 1.5$ suggests that the sources are more likely to be anthropogenic (Ghrefat et al., 2010). The results of the present study show EF values of Cu, Zn, Ni and Mn which are all < 2 (Table 5), indicating no or minimal enrichment. Pb is moderately enriched in all the locations while As is moderately enriched only in Ado-Ekiti clay samples. All the potentially hazardous elements considered in the study originate from the source rock except Pb which has $EF > 1.5$, indicating anthropogenic source.

The geo-accumulation index (I_{geo}) originally introduced and applied by Muller (1969) was used to evaluate the degree of elemental pollution in the clay soils from the study area. Mathematically, I_{geo} is given as (Zheng et al., 2010; Matini et al., 2011):

$$I_{geo} = \text{Log}_2 \left(\frac{C_n}{kB_n} \right) \quad (5)$$

Where C_n is the concentration of the potentially hazardous trace element (e.g Cu, Ni, Pb, etc) in the clay

sample, B_n is the geochemical background value in average shale (Turekian and Wedepohl, 1961) of element n and $k = 1.5$ is the background matrix correction factor introduced to account for possible differences in the background values due to lithogenic effects. The results of the geo-accumulation index obtained in this study indicate that Cu is moderately contaminated in Isan Ekiti clay with $I_{geo} = 1.09$ (Tables 5 and 6). Pb is moderately/strongly contaminated in all the sampled locations. The anthropogenic sources of Pb include; exhaust fumes from motor-vehicle, smelting activities, indiscriminate dumping of used lead acid batteries, etc.

Statistical analysis

Table 7 gives the descriptive statistics for the massive elemental concentrations of U, Th and K for all the measured clay samples. These includes; arithmetic means, median, standard deviation, maximum, minimum, skewness and Kurtosis, while the frequency distributions are presented in Figure 3.

The results of the Pearson correlation coefficients between the naturally occurring radionuclides and the major and trace elements are presented in Table 8. The results indicate a strong positive correlation between radioactive K and As. This radioactive K has a poor negative correlation with almost all the other elements except Ca, Se, Nb and

Pb. U correlates significantly only with Th and Sr at 95% confidence level. Th does not interact significantly with any of the major and minor elements. Fe correlates significantly with Ti, Cu, Zn, Mn, Ni, Se, Rb, Nb and Pb, whereas Ti has strong interactions with Cu and Mn. There exists a strong correlation between Ca and As; K and Sr; Cu and Zn, Mn, Ni, Se, Rb, Nb, Pb; Zn and Mn, Ni, Se, Rb, Nb, Pb; Mn and Se, Rb, Nb, Pb. Ni correlates strongly with Se, Rb, Nb, Pb while Se has a strong correlates with Rb, Nb, Pb. Strong interactions also exist between Pb and As. All the three radionuclides considered in this study are poorly correlated with the measured major and trace elements indicating different geochemical behavior. Positive correlations however exist between most of the elemental pairs in the clay samples suggesting the same source or co-contamination. Negative or inverse correlations between variables indicate that the variable pairs are derived from different origin and that such do not associate in their geochemical dynamics.

Conclusion

Radiometric and elemental investigations performed on clay soils reveal the presence of three naturally occurring radionuclides and fifteen major and trace elements. The results show that the radionuclides and elemental concentrations varied widely among the sampling locations. Most of the elements have higher concentrations than the baseline values. The concentrations of U (ppm), Th (ppm) and K (%) are comparable with results from other locations around the world and lower than the world average except U. Soil pollution in the present study was assessed using enrichment factor and geoaccumulation index values. The results indicate that the clay soil samples examined in this study are unpolluted with Cu, Zn, Ni, and Mn. Pb is moderately contaminated in all the sampling locations. The study shows that all the potentially hazardous elements originate from the source rock except Pb, which has EF > 1.5, indicating anthropogenic source.

Descriptive statistics and correlation analysis was carried out on the results in order to have a better understanding of the complex dynamics of the measured parameters. The Pearson correlation analysis shows poor interactions between radionuclides and elemental concentrations. Strong positive correlations were observed among most elemental pairs suggesting the same origin and similar geochemical behavior.

Competing interests

The authors declared that there is no competing interests.

Authors' contribution

IMO carried out the sample collection and drafted the manuscript. SMBO edited the drafted manuscript. OMO carried out the sample analysis. All authors read and approved the final manuscript.

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