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Variations in elemental and radiometric concentrations of soils around a mining site in Southwestern Nigeria

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Abstract

Soil samples from a mine site in Ijero, Ekiti State South-west Nigeria, were investigated for their elemental and radionuclides (^{40}K, ^{232}Th and ^{238}U) concentrations to assess the contaminations levels. Twenty (20) soil samples were randomly collected using Dutch stainless steel Auger around the mine sites but largely dictated by the miners activities and locations. Elemental and radioactivity (^{40}K, ^{232}Th and ^{238}U) components of the soils were determined using particle induced X-ray emission and Gamma spectrometers respectively. To assess the level of contamination and the possible anthropogenic impact, the pollution indices and the geo-accumulation indices of some elements were calculated. Twenty-six elemental (Na, Mg, Al, Si, Cl, K, Ca, Ti, V, Cr, Fe, Cu, Zn, Ga, Rb, Zr, Nb, Cd, Sn, Ba, Nd, Bi, Pb, Pa, Th and U) concentrations were quantified. Average concentrations of these toxic elements; V (327 µg g^{-1}), Cu (276 µg g^{-1}), Nb (806 µg g^{-1}), Cd (785 µg g^{-1}), Pb (394 µg g^{-1}), Th (473 µg g^{-1}) and U (500 µg g^{-1}) were particularly high, exceeding recommended values. Activity concentrations of the radionuclides ranged from 1 to 3, 4 to 10 and 415 to 15520 kBq kg^{-1} for ^{232}Th, ^{238}U, and ^{40}K respectively with an average exceeding world limit which could lead to possible radiological consequences. Geo-accumulation and the pollution risk factor studies revealed that Pb could pose significant potential health risk to the miners and ecosystem.

Keywords
Elemental, Pollution, Radiometric, Soil, Toxicity

Introduction

Artisanal mineral exploitation practices are basically the method of extraction which often leads to loss of other associated recoverable economic minerals and eventual contamination of ecosystem with mining tailings. The miners and ecosystem could be exposed to negative impacts of the more accessible. radionuclides and toxic trace metals (Olise et al. 2011, Isinkaye et al. 2013). This work is aimed at evaluating radionuclides (^{40}K, ^{232}Th and ^{238}U) and elemental concentrations of mineral hosted soils from a mining area at Ijero Ekiti, South-West Nigeria using Particle Induced X-ray Emission (PIXE) and Gamma spectro-analytical techniques. The cross-analysis of elemental and radiometric data provides useful tools for better understanding of the impacts of mining activities in the environment (Brai et al. 2006).

Materials and Methods

Study Area

Figure 1 shows the study site which is Ijero-Ekiti (7°49' N and 5°50' E) in the mineralogy map of Ekiti State Nigeria Southwestern Nigeria. The area is entirely situated within the tropics and characterized with high temperature and heavy rainfall. The geological formation of the area is precambrian basement and made of rock sequence vis-a-viz pegmatites, aplites, granitic rocks, charnokitic rocks, the quartzite series, gneisses and magnetites (Olarewaju 1981;UNAD 2009. The solid minerals mined in the study area are

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columbite-tantalite, quartz, kaolin, mica, feldspar, flint, foundry sand and cassiterite.

Sample Collection and Preparation

Seventeen (17) samples were collected randomly around the active Ijero mine site including two mineral ore and a control (obtained about 10 km away from the site) as well as three (3) samples which were obtained from the old and in-active Isan (IS) site. The sampling was largely dictated by the miners activities and locations and was done using the Dutch stainless steel Auger while the mineral ore samples were obtained from already dug-out materials. For the control sample, an undisturbed mining activity-free site was chosen.

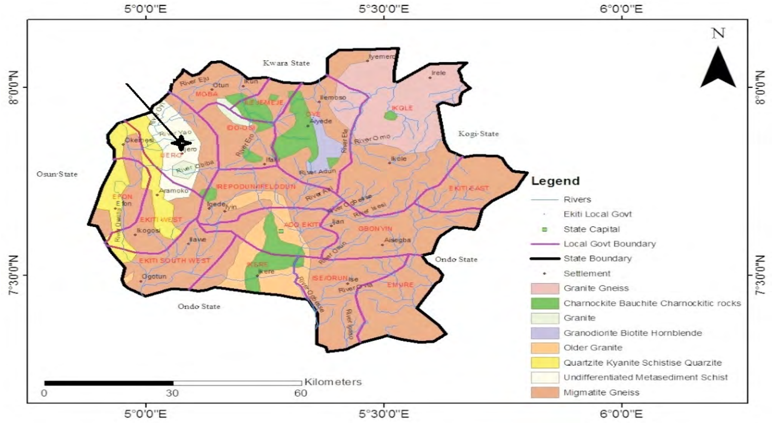

Figure 1. *Mineralogical map of Ekiti State showing the study site.*

To achieve homogeneous representation of soil samples, 5 to 10 sub-samples were taken from about 2 m x 2 m square plots on the specific collection points and that of the control. The sub-samples were homogenised and a representative sample taken from the mix. Samples were air dried under room temeperature to constant weight in order to ensure elimination of moisture and pulverised to fine particles using an Agate mortar with pestle. Prior to pulverization, Agate mortar and pestle were washed and rinsed with distilled water and dry-cleaned with 99 % purity ethanol to avoid cross contamination of the samples. From each sample, triplicate pellets of 13 mm diameter and about 1-3 mm thick were made with Spec-caps by applying 8 torr pressure using manual hydraulic pelletizer machine. The Obsidian Rock 278 certified reference material was also prepared in a similar way before PIXE analysis for quality control and assurance purposes.

PIXE set-up and analysis

PIXE analysis of the samples were performed using a particle beam from the NEC 5SDH 1.7 MV Tandem accelerator at Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Nigeria. It has an in-vacuum multi-purpose scattering chamber designed to perform particle Ion Beam experiments. The scattering chamber has a view port for monitoring the beam and with a variable collimator for beam size selections. Detector signals were shaped and amplified through a pulse height analysis and the energy spectrum was stored and displayed with a multi-channel analyzer. Each sample run was irradiated with H^+ beam of 2.5 MeV and a charge of 3.0 μC while the beam collimator was 4 mm diameter. A low beam current of 3 to 6 nA was maintained in order to ensure that the dead time remained below 10 %. The duration of the sample irradiation was about 10 to 20 minutes depending on the sample matrix. The target was positioned at 45 ° with respect to the beam normal and the characteristic X-rays were detected by a Si-Li detector (model ESLX 30 - 50, - 500 V). The detector has a beryllium window thickness of 25 μm, full width at half maximum (FWHM) energy of 150 eV, with the associated pulse processing electronics and a Canberra Genie 2000 (3.1) multichannel analyser (MCA) card interfaced to a PC. An absorber Kapton (90 μm thickness) was attached to the X-ray detector port in order to reduce high count rate and X-ray intensities of low Z elements as well as to suppress the spectrum background. Corrections for the suppressed peaks were made as reported (Olise et al., 2010a). For reliable calibration of the analytical system (viz. X-ray yield observed by the detector per unit charge per unit mass of the element) NIST Obsidian Rock 278 geological reference standard was

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used as quality control of the experimental procedure. X-ray spectra obtained from PIXE measurements were analyzed using thick target option of computer-coded GUPIXWIN (Campbell et al., 2010).

Gamma-ray spectroscopy

The activity concentrations of natural radioactivity in the selected samples were determined using a 7.62 cm × 7.62 cm NaI (Tl) detector surrounded with adequate lead shield that reduces background by a factor of approximately 95 %. The optimal counting of 25200 seconds were used and detection limits of the NaI (Tl) detector system were calculated as 6.77, 11.40, and 12.85 Bq kg^{-1} for ^{40}K, ^{232}Th, and ^{238}U, respectively. The activities of various radionuclides were determined in Bq kg^{-1} from the count spectra obtained from each of the samples using the gamma ray photo peaks corresponding to energy of 1120.3 keV (^{214}Bi), 911.21 keV (^{228}Ac) and 1460.82 keV (^{40}K) for ^{238}U, ^{232}Th and ^{40}K, respectively. After spectrum analysis, the count rates under each photopeak were used to calculate the activity concentration of each nuclide (Olise et al. 2010a, Olise et al. 2013) as show:

$$A_E = \frac{M_E \lambda_E N_A}{W_E} \qquad [1]$$

where, M_E is the fractional weight of nuclide E in the sample, W_E is the atomic weight of nuclide E (kg/mol), λ_E is the decay constant (s^{-1}) of the parent radioisotope and N_A is the Avogadro's number (6.023 x 10^{23} atoms/mol).

The absorbed dose rate, D (nGyh^{-1}) in air due to the radionuclides concentrations in the samples was calculated at a distance of 1 m above the ground level using (UNSCEAR 2000, Olise et al. 2011):

$$D = 0.042A_k + 0.666A_{Th} + 0.429A_U \qquad [2]$$

where, A_k, A_{Th} and A_U are the activity concentrations (Bq/kg) of ^{40}K, ^{232}Th and ^{238}U, respectively. Other radionuclides like ^{137}Cs and ^{90}Sr decay series were conviniently neglected, since they contribute very little to the total background dose (Leung et al. 1990, Olise et al. 2016).

To estimate the annual effective doses, we considered the conversion coefficient from the absorbed dose in air to effective dose and the indoor occupancy factor which their average numerical values could be a function of the age of resident population and climate change. In some studies, 0.7 Sv Gy^{-1} have been used as conversion coefficient for absorbed dose in air to effective dose received by adults while 0.2 and 0.8 have been used as outdoor and indoor occupancy factors respectively. This implies that on the average, 20% of time is spent outdoors around the world (UNSCEAR 2000). In summary, the populace at the study area could spend up to 60 % of their time outdoors (Olise et al. 2016) and the local miners and farmers with a 6 am to 4 or 6 pm mining or farming activities, could spend between 10 (42%) and 12 (50%) hours outdoors. Therefore, annual effective dose were determined by taking occupancy factor to be 0.4583 while outdoor effective dose rate (OEDR) was estimated as:

$$\begin{aligned} \text{OEDR (mSvy}^{-1}) = \text{D(nGyh}^{-1}) \cdot 24\text{hd}^{-1} \cdot 365.25\text{dy}^{-1} \cdot \\ 0.4583\text{(OCPF)} \cdot 0.7\text{SvGy}^{-}1\text{(CONVC)} \cdot 10^{-6} \end{aligned} \qquad [3]$$

where, OCPF and CONVC are the occupancy factor and conversion coefficient, respectively. Since the indoor and outdoor occupancy factors need to sum up to 1.0 in accounting for 100 % of the exposure group's time, an indoor factor of 1 - 0.4583 = 0.5417 was used to calculate the indoor effective dose rate (IEDR):

$$\begin{aligned} \text{IEDR (mSvy}^{-1}) = \text{D(nGyh}^{-1}) \cdot 24\text{hd}^{-1} \cdot 365.25\text{dy}^{-1} \cdot \\ 0.5417\text{(OCPF)} \cdot 0.7\text{SvGy}^{-}1\text{(CONVC)} \cdot 10^{-6} \end{aligned} \qquad [4]$$

Data Analysis

The results obtained from PIXE analysis were subjected to further analysis in-order to determine the Geo-accumulation Index (I_{geo}) and Potential Ecological Risk Index of some selected metals in the study sites.

I_{geo}

I_{geo}, was introduced by Muller, (1969) for determining the extent of metal accumulation in sediments, and has been widely used in various studies. I_{geo} is mathematically expressed as:

$$I_{geo} = \frac{\text{Log}_2\, C_n}{1.5\, B_n} \qquad [5]$$

where, C_n is the concentration of element in the sediment, B_n is the geochemical background value (Taylor, 1985). The constant 1.5 was incorporated in the relationship to account for possible variations in background data due to lithogenic effects. The Igeo scale consists of seven grades (0 to 6) ranging from unpolluted to highly polluted (Table 1).

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I_{geo} class	I_{geo} value	I_{geo} quality
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} <1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} <2$	Moderately contaminated
3	$2 < I_{geo} <3$	Moderately to heavily contaminated
4	$3 < I_{geo} <4$	Heavily contaminated
5	$4 < I_{geo} <5$	Heavily to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

Table 1. *Pollution grades of geo-accumulation index of metals.*

Potential Ecological Risk Index

The Potential Ecological Risk Index (RI) was introduced by Hakanson (1980) to assess the degree of heavy metal pollution in soil, according to the toxicity of metals and the response of the environment. The steps involved to calculate the potential ecological risk index is listed below.

$$F_i = \frac{C^i_n}{C^i_o} \qquad [6]$$

$$E^i_i = \qquad T^i_r \cdot F_i \qquad [7]$$

$$\sum_{i=1}^{n} E_i = E_1 + E_2 + E_3 + \ldots\ldots\ldots\ldots\ldots E_n \qquad [8]$$

where, F_i is the single metal pollution index; C^i_n is the average concentration of metal in the samples; C^i_o is the reference value for the metal; E^i_i is the monomial potential ecological risk factor; T^i_r is the metal toxic response factor according to Hakanson (1980). RI is the potential ecological risk caused by the overall contamination and categorized as shown in Table 2.

E^i_i value	Grades of ecological risk of metals	Risk Index (RI)	Grades of the environment
$E^i_i < 40$	low risk	RI < 110	low risk
$40 \leq E^i_i < 80$	moderate risk	110 ≤ RI ≤ 200	moderate risk
$80 \leq E^i_i < 160$	considerable risk	200 ≤ RI ≤ 400	considerable risk
$160 \leq E^i_i < 320$	high risk	400 ≤ RI	very high risk
$320 \leq E^i_i$	very high risk		

Table 2. *Indices and grades of potential ecological risk of toxic metals contamination.*

Results and Discussion

Quality assurance

The results of the Obsidian rock 278 standard reference material analysed under the PIXE protocol are presented in Table 3 alongside with their corresponding certified reference values.

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Elements	Experimental values (µg g^{-1})	Certified reference values (µg g^{-1})	PIXE Efficiency (%)
Na	35810	35900	99.75
Mg	1400	1390	100.72
Al	74630	74900	99.64
Si	341660	341436	100.07
K	34430	34530	99.71
Ca	7020	7025	99.93
Ti	1470	1468	100.14
Mn	390	403	96.77
Cu	5.9	5.9	100.00
Fe	14270	14268	100.01
Rb	55	55	100.00
Sr	62	63.5	97.64
Ba	1145	1140	100.44

Table 3. *Results of NIST obsidian rock 278 standard reference material.*

The results compared well with the certified values. PIXE analysis results of thirteen elements (Na, Mg, Al, Si, K, Ca, Ti, Mn, Cu, Fe, Rb, Sr and Ba) recorded above 96 % efficiency in each of the elements detected. For instance, the PIXE efficiecy for Na, Si, Ca, Cu and Ba were 99.75, 100.07, 99.93, 100.00, and 100.44 respectively. However, Mn was underestimated by 4 % probably as a result of the 90 µm thickness Kapton filter which was placed before the Si-Li detector. The filter helped to reduce the background resulting from the high intensity of the light elements constituting the matrix (Olise et al. 2010b). The results of other elements were comparable to certified values, which implies the reliability and reproducibility of the PIXE procedure.

Average elemental concentrations (µg g^{-1})

The values of the average concentration of twenty-six elements (Na, Mg, Al, Si, Cl, K, Ca, Ti, V, Cr, Fe, Cu, Zn, Ga, Rb, Zr, Nb, Cd, Sn, Ba, Nd, Pb, Bi, Pa, Th, U) detected and analyzed in the samples are presented in Tables 4a and 4b.

Measurement errors were typically in the range of ±1 to 10 % for most species due to fundamental fitting parameters and efficiency callibrations. Figure 2 showed the spectrum of a typical soil sample with associated elements.

Average concentrations for Al (29661 µg g^{-1}), Si (60098 µg g^{-1}), K (14535 µg g^{-1}), Ca (1363 µg g^{-1}), Fe (44227 µg g^{-1}), Ti (3310 µg g^{-1}) and Nd (10282 µg g^{-1}) were the most abundant elements, apparently reflecting their crustal nature. Interestingly, average concentration of Ba (6988 µg g^{-1}), Rb (3328 µg g^{-1}), and Sn (2011 µg g^{-1}) were also prominent. However, toxic elements; V, Cd, Ba and Pb had no unique trend. Vanadium has an average of 330 µg g^{-1}, a value higher than worldwide average of 100 µg g^{-1} in soils (Kabata-Pendias and Pendias 1992). Other toxic elements Cd, Ba and Pb have an average concentration values of 785, 6990 and 394 µg g^{-1}, respectively.

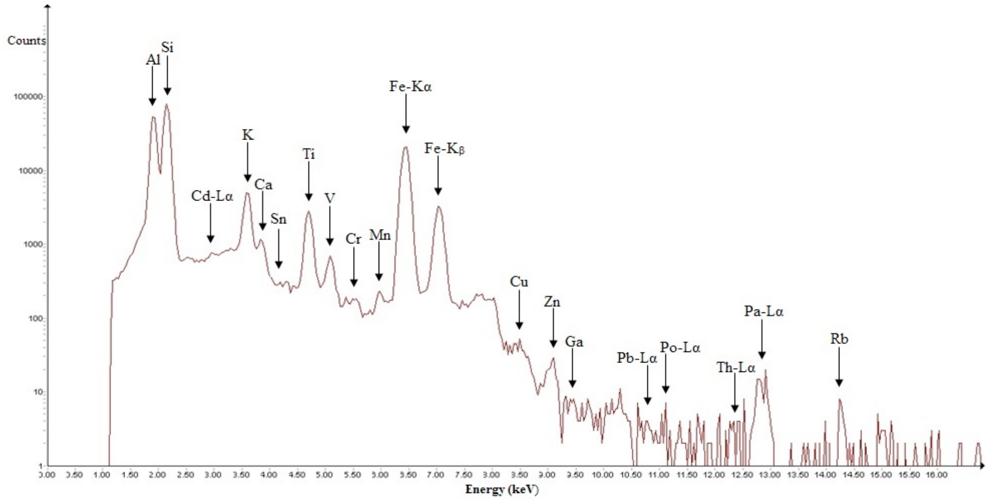

Figure 2. *PIXE spectrum of a typical sample.*

Elements/ Sample ID	Na	Mg	Al	Si	Cl	K	Ca	Ti	V	Cr	Fe	Cu	Zn
IJGMQ1	ND	168 ±26	43157 ±2	37030 ±2	107 ±48	14660 ±2	256 ±17	328 ±17	ND	ND	10710 ±1	ND	ND
IJGMQ2	ND	121 ±42	38314 ±2	48470 ±2	120 ±39	1600 ±4	ND	ND	ND	ND	2100 ±2	130 ±25	120 ±20
IJGMQ3	ND	ND	27729 ±2	41390 ±2	ND	3655 ±3	ND	ND	ND	ND	2729 ±1	ND	130 ±27
IJGMQ4	ND	128 ±34	31848 ±2	56448 ±1	130 ±37	8915 ±2	312 ±15	1082 ±5	127 ±30	113 ±24	38160 ±1	223 ±24	163 ±25
IJGMQ5	384 ±8	ND	31649 ±2	63628 ±2	ND	3630 ±3	1105 ±5	1582 ±4	ND	167 ±14	4660 ±2	ND	ND
IJGMQ6	ND	ND	31547 ±2	54825 ±2	113 ±39	3776 ±3	ND	ND	192 ±21	ND	59033 ±1	208 ±30	133 ±32
IJGMQ7	ND	ND	35404 ±2	57270 ±2	ND	1712 ±4	385 ±10	3091 ±3	ND	93 ±21	2280 ±2	ND	ND
IJGMQ8	ND	ND	36194 ±2	58582 ±2	ND	13110 ±2	128 ±35	93 ±24	ND	ND	9000 ±1	ND	237 ±15
IJGMQ9	ND	ND	31496 ±2	60990 ±2	ND	47766 ±1	405 ±17	113 ±34	ND	ND	5245 ±1	ND	153 ±24
IJGMQ10	348 ±8	ND	23343 ±2	80196 ±2	ND	15772 ±2	2192 ±4	172 ±18	ND	110 ±20	15324 ±1	ND	164 ±20
IJGMQ11	ND	ND	28262 ±2	73444 ±2	ND	10662 ±2	800 ±7	ND	ND	204 ±11	6134 ±1	ND	97 ±23
IJGMQ12	ND	ND	33363 ±2	58740 ±2	ND	21034 ±2	337 ±17	357 ±12	106 ±30	150 ±18	12906 ±1	131 ±25	125 ±23
IJGMQ13	ND	ND	37967 ±2	51233 ±2	96 ±16	3677 ±3	83 ±40	ND	ND	ND	10197 ±1	ND	136 ±20
IJGMQ14	255 ±9	ND	24961 ±2	71334 ±1	ND	10930 ±2	3523 ±3	179 ±23	ND	116 ±30	15848 ±1	ND	371 ±17
Feldspar	224 ±12	ND	25936 ±2	67547 ±2	ND	16830 ±2	472 ±13	624 ±8	113 ±31	223 ±15	24090 ±1	141 ±40	2232 ±4
Mica	ND	ND	36345 ±2	48167 ±2	ND	59887 ±1	331 ±22	ND	ND	ND	41312 ±1	ND	2640 ±3
IS1	ND	422 ±9	22176 ±2	55030 ±1	118 ±38	16350 ±2	1080 ±6	7340 ±2	408 ±13	ND	154010 ±1	243 ±30	333 ±15
IS2	ND	ND	15054 ±2	57827 ±1	163 ±38	16515 ±2	8086 ±2	14796 ±2	723 ±9	ND	164464 ±1	364 ±20	377 ±13
IS3	468 ±12	671 ±8	22118 ±2	59128 ±2	144 ±37	16473 ±2	2576 ±3	10948 ±2	570 ±12	ND	177740 ±1	552 ±14	340 ±16
Control	ND	ND	16367 ±2	100675 ±1	ND	3750 ±3	1098 ±5	5632 ±2	373 ±13	ND	104038 ±1	493 ±14	385 ±13
Range	224⇔ 468	108⇔ 671	15054⇔ 43157	37027⇔ 100675	96⇔ 163	1600⇔ 59887	83⇔ 8086	93⇔ 14796	106⇔ 723	93⇔ 223	2100⇔ 177740	130⇔ 552	97⇔ 2640
Mean	336 ±44	270 ±94	29661 ±1670	60098 ±3140	124 ±8	14535 ±3325	1363 ±481	3310 ±1251	327 ±82	147 ±17	44227 ±12885	276 ±53	478 ±181

ND = means "Not Detected"

Table 4a. *Average elemental concentrations in the samples (μg g^{-1}).*

Elements/ Sample ID	Ga	Rb	Zr	Nb	Cd	Sn	Ba	Nd	Pb	Bi	Pa	Th	U
IJGMQ1	266 ±13	514 ±27	ND	ND	ND	ND	ND	11310 ±124	763 ±28	ND	996 ±41	ND	341 ±84
IJGMQ2	244 ±19	629 ±19	ND	4448 ±10	ND	ND	ND	ND	ND	ND	ND	ND	ND
IJGMQ3	192 ±18	379 ±30	ND	184 ±90	ND	ND	ND	ND	ND	ND	450 ±82	324 ±60	ND
IJGMQ4	171 ±22	1191 ±14	ND	ND	776 ±132	ND	ND	ND	177 ±74	ND	ND	ND	ND
IJGMQ5	130 ±23	266 ±38	ND	240 ±74	ND	ND	7240 ±108	ND	ND	ND	ND	ND	ND
IJGMQ6	202 ±20	603 ±24	220	ND	793 ±122	1885 ±88	ND	ND	284 ±48	ND	620 ±73	640 ±40	ND
IJGMQ7	178 ±19	ND	ND	ND	ND	ND	7010 ±100	ND	ND	ND	548 ±50	ND	ND
IJGMQ8	304 ±13	3786 ±7	ND	380 ±50	ND	ND	ND	ND	ND	ND	ND	ND	ND
IJGMQ9	162 ±28	19263 ±3	ND	337 ±68	ND	ND	ND	ND	ND	ND	ND	397 ±102	ND
IJGMQ10	146 ±20	1523 ±12	ND	274 ±65	ND	3685 ±46	ND	ND	ND	ND	ND	ND	487 ±67
IJGMQ11	120 ±23	929 ±17	ND	290 ±68	ND	ND	6712 ±110	6150 ±238	250 ±36	186 ±51	ND	ND	ND
IJGMQ12	151 ±20	2496 ±9	408	ND	ND	1337 ±115	ND	ND	ND	ND	1210 ±38	342 ±60	ND
IJGMQ13	200 ±17	2947 ±8	ND	ND	ND	1137 ±133	ND	ND	ND	ND	ND	ND	402 ±80
Mica	665 ±10	18661 ±3	ND	860 ±34	ND	ND	ND	12670 ±110	ND	ND	ND	ND	765 ±64
IS1	144 ±30	698 ±26	734 ±32	ND	ND	ND	ND	ND	701 ±43	301 ±76	ND	ND	ND
IS2	147 ±23	1005 ±16	1553 ±18	427 ±46	ND	ND	ND	ND	403 ±46	252 ±50	ND	428 ±58	ND
IS3	131 ±27	866 ±19	1238 ±20	ND	ND	ND	ND	ND	ND	ND	676 ±60	ND	ND
Control	ND	ND	683 ±34	ND	ND	ND	ND	ND	181 ±83	ND	ND	710 ±30	ND
Range	120⇔ 665	265⇔ 19263	220⇔ 1553	184⇔ 4448	776⇔ 793	1137⇔ 3685	6712⇔ 7241	6151⇔ 12671	177⇔ 763	186⇔ 301	450⇔ 1211	324⇔ 710	41⇔ 765
Mean	206 ±29	3328 ±29	806 ±206	806 ±410	785 ±9	2011 ±580	6988 ±153	10282 ±1424	394 ±92	246 ±34	750 ±120	473 ±66	500 ±94

ND = means "Not Detected"

Table 4b. *Average elemental concentrations in the samples (μg g^{-1}).*

These values exceeded the average geochemical background data of 0.53 μg g^{-1} (Kabata-Pendias and Pendias 1992), 4 μg g^{-1} (Turekian and Wedepohl 1961) and 20 μg g^{-1} (Kabata-Pendias and Pendias 1992) for Cd, Ba and Pb, respectively. These toxic elements, depending on their chemical form, could pose a potential health risk to the miners and the exposed populace. While the impact of radionuclides are probabilistic, those of toxic metals are deterministic and attracts immediate consequences at elevated levels. Some possible health risks have been identified to include hyperkeratosis, hyperpigmentation (Tseng 1977), impairment of reproduction and lipid metabolism, extrasystoles and reduced level of blood cholesterol (Vouk 1979). High level of Pb poisoning and eventual death resulting from artisanal mining activities have been reported in two towns in Northern Nigeria (Olise et al. 2016).

From the study, the identified potentially toxic elements can be used as fingerprint for immediate or near future evaluation of artisanal mining-related impacts in the study area. Such impacts could include but not limited to chronic human metal poisoning from consumption of plant and animal materials enriched in the metals. Interestingly, trace metal concentrations observed in the control samples were lower than values observed in the other samples, thus an indication of the influence of mining activity on soil composition.

The calculated average I_{geo} values for the samples are summarized in Table 5. From the table, I_{geo} values for the low Z elements (Na to Fe) ranged from -0.03 (Cr) to -6.98 (Na). The negative values could be an indication that the study soils are uncontaminated of those elements. Conversely, the average I_{geo} of Cu, Zn, Rb, Zr, Ba, Pb, Th and U ranged from moderately to extremely contaminated classess. For instance, Cu (1.74) and Zr (1.70) were in the moderately contaminated class while Zn was in the moderately to heavily contaminated class. Equally, Rb (4.62), Ba (4.22), and Pb (4.34) were found in the heavily to extremely contaminated class while Th and U with I_{geo} values of 6.49 and 8.41 were in the extremely contaminated class. High average I_{geo} values reported for Rb, Ba, Pb, Th and U is worrisome and calls for further investigations on the study sites.

Element	Concentrations (µg/g)	Crustal Rock (µg/g) (Taylor, 1964)	Geo-accumulation Index (I_{geo})	Potential Ecological Risk Indices
Na	336	28300	-6.98	0.01
Mg	270	20900	-6.86	0.01
Al	29661	81300	-2.04	0.36
Si	60098	277200	-2.79	0.22
Cl	124	130	-0.65	0.95
K	14535	25900	-1.42	0.56
Ca	1363	36300	-5.32	0.04
Ti	3310	4400	-1.00	0.75
V	327	135	0.69	2.42
Cr	147	100	-0.03	1.47
Fe	44227	50000	-0.76	0.88
Cu	276	55	1.74	5.02
Zn	478	70	2.19	6.83
Ga	206	N.D.	N.D.	N.D.
Rb	3328	90	4.62	36.98
Zr	806	165	1.70	4.88
Nb	806	N.D.	N.D.	N.D.
Cd	785	N.D.	N.D.	N.D.
Sn	2011	N.D.	N.D.	N.D.
Ba	6988	250	4.22	27.95
Nd	10282	N.D.	N.D.	N.D.
Pb	394	13	4.34	30.31
Bi	246	N.D.	N.D.	N.D.
Pa	750	N.D.	N.D.	N.D.
Th	473	3.50	6.49	135.14
U	500	0.98	8.41	510.20

N.D. means "not detected"

Table 5. *Average* EF, I_{geo} *and potential ecological risk indices.*

Table 5 also depicts the average ecological risk assessment of toxic metals in the study area. It was found that the average F_i ranged from 0.01 to 510 while the average monomial risk factor (E^i_r) of the toxic metals; Cr (2.94), Cu (25.09) and Zn (6.83) were below 40 indicating that these metals posed low risk to environment. There was only one monomial ecological risk above 100, which is Pb (E^i_r = 151.54) indicating moderate risk. In order to quantify the overall potential ecologicak risk of observed metals, RI was calculated as the sum of all the six risk factors. RI could provide information regarding sensitivity of local ecosystem to the toxic metals and also represent ecological risk that resulted from the overall contamination. The RI values for the calculated metals were in the order Pb (81.3 %) > Cu (13.5 %) > Zn (3.7 %) > Cr (1.7 %). Overall, Pb contributed 81.3 % of the total potential ecological risk.

Elemental Concentrations of the Radionuclides

As expected, ^{40}K was present in all the samples while ^{232}Th and ^{238}U were detected in few samples. The concentration of ^{40}K ranged from 1600 to 59890 µg g^{-1} with an average concentration value of 14540 µg g^{-1} (Table 4). Potassium is an essential constituent of many minerals including feldspar, mica, clay and, especially, in granitic rock types (Miller et al. 2002). Thorium - 232 concentration ranged from 324 to 710 µg g^{-1} and has an average of 473 µg g^{-1}. The solubility of Th in soils has been reported to likely increase with several organic acids (Mirza and Ismail 2007). This factor might therefore be responsible for the detection of thorium in few of the samples. Uranium-238 concentration ranged from 341 to 765 µg g^{-1} with an average concentration value of 500 µg g^{-1}. Rock forming minerals like hornblende, pyroxene, feldspar, biotite, muscovite, olivine, allanite, opatite has been reported to have typical levels of uranium (Miller et al. 2002). It should therefore be expected for the samples, especially those from Ijero, to contain appreciable level of U. The detection of U in only few of the samples might be largely due to its labile nature in the two-mica granite type common in the study area and hence, could be dissolved in groundwater during weathering (Olise et al. 2016).

The elevated levels of the radionuclides, as observed in this study, could expose the miners and ecosystem to huge health risk through inhalation, ingestion and surface run off. Radiological consequences of the elevated levels of the radionuclides have been reported to include target of bones and lungs, kidney failure, termination in muscular apathy, progressive emaciation, excretory disfunction, increased incidence of leukaemia, coma and worst case scenario of death (Keith et al. 2013). The area can therefore be said to be potentially radiologically unsafe from hazardous natural radiation sources.

Conversion of Elemental Concentrations to Activity Concentrations (kBq/kg)

From the elemental concentrations data, the required radionuclides activity concentrations were obtained from equation (1). The average activity concentrations of ^{40}K, ^{232}Th and ^{238}U, calculated from the elemental concentration data are presented in Table 6.

It ranged from 415 to 15520 kBq/kg for ^{40}K, 4 to 10 kBq/kg for ^{238}U and 1 to 3 kBq/kg for ^{232}Th with the mean values of 3770, 2 and 6 kBq/kg, respectively. When compared with the worldwide reported average activity concentrations of 400 Bq/kg for ^{40}K, 35 Bq/kg for both ^{232}Th and ^{238}U in soil (UNSCEAR 2000), the obtained activity concentrations were higher than the average values by several orders of magnitude. Also, the obtained activity concentrations levels of the natural radionuclides were higher than those earlier reported (Faweya and Oniya 2012, Oladipo et al. 2014, Olise et al. 2016) at simillar sites. This could be reflecting the total elemental or non-isotopic analysis nature of the PIXE procedure from which we calculated the activity concentrations. Furthermore, the PIXE procedure has a low detection limit and adequate spectrum peaks detector resolution. In addition, there is no sample self-absorption, interference, geometrical and density correction problems typical of gamma spectrometry employed in the reported studies. Though, the possible variation in sample type and wide departure in degree of representativeness could be a factor for the wide differences in the activity concentrations, its contribution should be minimal judging from the most possible similarity of samples in this work with those of Olise et al. (2016).

The calculated activity concentrations of the natural radionuclides of ^{40}K, ^{232}Th and ^{238}U showed that the potential exposures would be higher than the limits for the public. This could be a concern and should be of interest to the various levels of government. This is because the present way of mining would continue to concentrate the radionuclides and hence increased activity. There is also the likelihood of increased exposure by making the radioactive material more accessible to the populace. Therefore, the use of materials from radionuclides-rich mining areas for building and any other developmental projects needs to be discouraged.

Sample ID	^{40}K	^{232}Th	^{238}U
IJGMQ1	3799.61 ±0.40	ND	4.20 ±1.00
IJGMQ2	414.46 ±1.14	ND	ND
IJGMQ3	947.38 ±0.63	1.33 ±0.24	ND
IJGMQ4	2310.77 ±0.51	ND	ND
IJGMQ5	940.64 ±0.80	ND	ND
IJGMQ6	978.74 ±0.71	2.62 ±0.16	ND
IJGMQ7	443.75 ±101.35	ND	ND
IJGMQ8	3398.89 ±0.45	ND	ND
IJGMQ9	12380.95 ±0.31	1.63 ±0.42	ND
IJGMQ10	4088.10 ±0.43	ND	6.01 ±0.83
IJGMQ11	2763.59 ±0.46	ND	ND
IJGMQ12	5452.01 ±0.39	1.40 ±0.24	ND
IJGMQ13	953.08 ±0.67	ND	4.97 ±0.99
IJGMQ14	4238.18 ±0.52	ND	ND
Feldspar	4362.60 ±0.42	ND	ND
Mica	4280.69 ±0.31	1.75 ±0.24	ND
IS1	15522.71 ±0.40	ND	9.45 ±0.78
IS2	2833.06 ±0.43	ND	ND
IS3	4269.80 ±0.48	ND	ND
Control	971.74 ±0.73	2.91 ±0.12	ND
Range	414.46 - 15522.71	1.33 - 2.91	4.21 - 9.45
Mean	3767.54 ±861.91	1.94 ±0.27	6.16 ±1.16

Table 6. *Average activity concentration of radionuclides in the samples (kBq/kg).*

Dose Rates

Table 7 shows the average outdoor absorbed dose rates (OADR), the outdoor effective dose rates (OEDR), the indoor effective dose rates (IEDR) and the total annual effective dose rates (AEDR) due to the measured radionuclides. The outdoor absorbed dose rates due to the radionuclides ranged from 1.74 to 69.25 μGy h^{-1}, with a mean of 16.73 μGy h^{-1}. A higher mean dose rate was observed in comparison with the world average of 0.06 μGy h^{-1} (UNSCEAR 2000). It means that the calculated outdoors absorbed dose rate is very high at the mine sites. Thus, the miners could be exposed to high dose rate which poses radiological health threat. The average annual outdoor effective dose (Table 5) ranged from 5 to 198 mSv, with a mean of 48 mSv. A higher mean value was observed in comparison with the worldwide average outdoor exposures of 0.06 mSv (UNSCEAR 2000).

The annual indoor effective doses from the external exposure to γ-rays emitted from the radionuclides in the soil samples, if used as building materials, ranged from 6 to 230 mSv, with a mean of 55 mSv. This average is higher than the 0.41 mSv worldwide average of indoor exposures (UNSCEAR 2000). The sum of the outdoor and indoor annual effective doses, which is the total annual effective dose (Table 5), ranged from 11 to 425 mSv, with a mean of 103 mSv. A higher effective dose was observed in comparison with the worldwide average of 0.48 mSv (UNSCEAR 2000). The measured absorbed dose rates and the effective doses in this study stands high compared with those of the earlier studies on the study areas and other parts of the country. The calculated value was higher than the mean annual effective outdoor value of 0.07 mSvy^{-1} obtained from the mica site (Faweya and Oniya 2012) and also higher than the 0.04 mSvy^{-1} determined in the uncontaminated soil samples in Ijero (Ajayi 2002).

The calculated high absorbed dose rate in outdoor air at these sites implies exposure of the vulnerable population to a high dose rate, especially from fixed sources like buildings, with all the radio-sensitive tissues at risk. To protect the workers and the public, further monitoring of the sites should be carried out and controlled to avoid possible radiological impact to the population. Although the sites are still under some vegetative cover so that re-entrainment of particles from the waste is minimal, proper measures should be taken to check the dose assessment and leaching of U into the water bodies and migration of Th in mineral fragments. The leaching of U and migration of Th exposes the residents to further impact by ingestion, apart from direct exposure to radiation. Several organs of the body are potential targets of radio-toxic radionuclide such as Th that could lead to several health conditions. The use of soil from the mining areas for developmental projects such as buildings should be monitored in view of the absence of detailed studies on the indoor radiation dose and its effect for prolonged exposure.

Sample ID	OADR (nGy h^{-1})	OEDR (mSv)	IEDR (mSv)	TEDR (mSv)
IJGMQ1	17.6 ± 4.30	50.67 ± 12.27	58.30 ± 14.11	108.07 ± 26.38
IJGMQ2	1.74 ± 0.05	4.97 ± 0.14	5.72 ± 0.16	10.69 ± 0.30
IJGMQ3	4.87 ± 1.62	13.88 ± 4.62	15.97 ± 5.32	29.85 ± 9.94
IJGMQ4	9.71 ± 0.02	27.69 ± 0.06	31.86 ± 0.07	59.55 ± 0.13
IJGMQ5	3.95 ± 0.03	11.27 ± 0.09	12.97 ± 0.10	24.24 ± 0.19
IJGMQ6	5.86 ± 1.10	16.71 ± 3.14	19.22 ± 3.61	35.93 ± 6.75
IJGMQ7	1.86 ± 4.30	5.32 ± 12.27	6.12 ± 1.12	11.44 ± 26.39
IJGMQ8	14.28 ± 0.02	40.73 ± 0.06	46.86 ± 0.07	87.59 ± 0.13
IJGMQ9	53.09 ± 2.81	151.47 ± 8.02	174.30 ± 9.22	325.77 ± 17.24
IJGMQ10	19.75 ± 3.58	56.35 ± 10.21	64.83 ± 11.75	121.18 ± 21.96
IJGMQ11	11.61 ± 0.02	33.12 ± 0.06	38.11 ± 0.07	71.23 ± 0.13
IJGMQ12	23.83 ± 1.61	67.99 ± 4.59	78.23 ± 5.29	146.22 ± 9.88
IJGMQ13	6.14 ± 4.28	17.50 ± 12.21	20.14 ± 4.05	37.64 ± 6.26
IJGMQ14	17.80 ± 0.02	50.79 ± 0.06	58.43 ± 0.07	109.22 ± 0.13
Feldspar	18.32 ± 0.02	52.28 ± 0.06	60.15 ± 0.07	112.43 ± 0.13
Mica	19.15 ± 0.16	54.63 ± 0.46	62.85 ± 0.53	117.48 ± 0.99
IS1	69.25 ± 3.36	197.59 ± 9.59	227.30 ± 11.03	424.90 ± 20.62
IS2	11.90 ± 0.02	33.95 ± 0.06	39.06 ± 0.07	73.01 ± 0.13
IS3	17.93 ± 0.02	51.17 ± 0.06	58.87 ± 0.07	110.04 ± 0.13
Control	6.02 ± 0.81	17.17 ± 2.31	19.76 ± 2.69	36.93 ± 5.00
Average	16.73 ± 1.41	47.76 ± 4.02	54.95 ± 4.62	102.72 ± 8.64
Worldwide average	0.06	0.06	0.41	0.3 - 0.60

Table 7. *Average outdoor absorbed dose rates* (AADR), *outdoor effective dose rate* (OEDR*), indoor effective dose rates* (IEDR) *and total effective doses* (TEDR).

Conclusion

This work presents a study of the elemental analysis, radiometric, geoacumulation and toxicity potential risk indices of soil and ore samples from artisanal mining corridors in South West Nigeria. The work was performed via reconnaisance survey, field sampling, laboratory experiment and mathematical analysis. Twenty-six elements (Na, Mg, Al, Si, Cl, K, Ca, Ti, V, Cr, Fe, Cu, Zn, Ga, Rb, Zr, Nb, Cd, Sn, Ba, Nd, Bi, Pb, Pa, Th and U) were detected by PIXE technique. The elemental concentrations of most toxic elements, V (327 µg g^{-1}), Cu (276 µg g^{-1}), Nb (806 µg g^{-1}), Cd (785 µg g^{-1}), Pb (394 µg g^{-1}), Th (473 µg g^{-1}) and U (500 µg g^{-1}) were particularly high, exceeding World Health Organization's tolerance limit. The assessment of I_{geo} indicated that the soil was moderately contaminated by Cu and Zr, and Pb. Igeo of Rb, Ba and Pb depicts moderately to heavily contamination while Th and U displayed extremely contaminated class. Again, the monomial potential ecological risk factor of only Pb was in the moderately risk class. The concentrations of three radionuclides (^{40}K, ^{232}Th and ^{238}U) were established and their activity concentrations were higher than those of earlier studies as well as UNSCEAR 2000 values by several orders of magnitude. The study concluded that heavy metal pollutions from the mining sites poses great hazard to man and the nearby agricultural soils.

Disclosure statement

No potential conflict of interest was reported by the authors

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