Research Article

Correlations of ^{226}Ra and ^{222}Rn activity concentrations in surface soil and groundwater of basement complex geological area of southwest Nigeria

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Abstract
The quantitative evaluations of naturally occurring radioisotopes in environmental media have provided significant information on the geological and radiological characteristics of different environments around the world. In furtherance to a preliminary study within southwest Nigeria set out to determine the distribution of ^{222}Rn in groundwater and soil gas, the present study employed a well-shielded NaI(Tl) and RAD 7 detectors to determine activity concentrations of ^{226}Ra and ^{222}Rn in the media. Samples were collected from 100 sampling sites spatially distributed within the study area. Multivariate statistics were employed to extract the relationships between the activity concentrations of ^{226}Ra and ^{222}Rn in order to ascertain their origin and behavior in the basement complex geological area of southwest Nigeria. The mean activity concentration of ^{226}Ra falls below the world average value of 35 Bq kg^{-1} in soil as reported by UNSCEAR, and ^{222}Rn mean activity concentration is lower than 100 Bq l^{-1} recommended by WHO and European Commission as the criterion level in utility water for the members of the public. It can therefore be concluded that there is no significant radiological risks to the environment and human health due the presence of the measured radionuclides in soil and groundwater.

Keywords Radium · Radon · Radiological risks · Basement complex geology

1 Introduction

Man is continuously affected by the radiation present in the earth's terrestrial system due to the presence of natural radionuclides in soil and water [1, 2]. Groundwater serves as a major source of drinking water especially in developing countries where access to potable water is scarce. The natural radionuclides present in soil and groundwater are sources of internal and external radiation exposures to man with the potential of adverse health effects. Generally, sources of naturally occurring radionuclides are classified into three groups based on their origin, which include the cosmic radiation, cosmogenic and primordial radionuclides [3]. The primordial radionuclides are radionuclides of terrestrial origin which have existed on earth since its formation and are characterized by their long half-lives. They include radionuclides in the decay series of ^{238}U ($T_{1/2} = 4.51 \times 10^9$ years) and ^{232}Th ($T_{1/2} = 1.39 \times 10^{10}$ years) decay series and non-series ^{40}K ($T_{1/2} = 1.3 \times 10^9$ years) [4]. Terrestrial radiations from primordial radionuclides in the ^{238}U and ^{232}Th decay series and ^{40}K contribute about 84% of man's exposure to radiation from natural sources [3].

Man is exposed externally to radiation from NORMs due to the emission of gamma radiation from the radionuclides in the ^{238}U and ^{232}Th decay series and from ^{40}K in soil and building materials [5]. However, internal exposure results when the NORMs are ingested in food and water or when they are inhaled from air. As per radiation exposure due to the presence of NORMs in groundwater, the radionuclides in the uranium decay series are of greater concern due to

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their relative solubility in water as compared to those in the thorium series [6]. ^{226}Ra and ^{222}Rn belong to the uranium decay series, and they both decay by alpha emission with half-lives of 1622 years and 3.85 days, respectively [7]. In Nigeria, there are two distinct geological settings [8, 9], which are the sedimentary basin, which is predominant in the south–east, south–south and north–east regions of the country, and the basement complex, which is predominant in the south–west and parts of north–west and north–centre regions (Fig. 1 as modified from [10, 11]). Due to the presence of granitic rock formations in the basement complex areas, it has been observed that the areas fall within region with high background radiation and rich in uranium mineralization [12, 13]. Preliminary studies by the authors within the study area assessed the spatial distribution of ^{222}Rn in both groundwater and soil gas [14]. Since ^{226}Ra is a tracer to ^{222}Rn being its immediate parent radionuclide, the present research effort is therefore aimed at measuring and correlating the activity concentrations of ^{226}Ra and ^{222}Rn in soil and groundwater samples in the area so as to ascertain their origin and behavior in the basement complex geological area of southwest Nigeria in furtherance to the published preliminary studies in [14]. These will help in understanding their mobility and transportation mechanisms within various geological media.

2 Materials and methods

2.1 Collection and preparation of samples

Soil and groundwater samples were randomly collected from rural and urban settlements in the study area for analysis. At the collection points, 100 samples each of soil and groundwater were collected for gamma spectrometry in order to determine the activity concentration of ^{226}Ra. Continuous radon measurements were performed on the groundwater samples to determine ^{222}Rn activity concentration using RAD7-H_2O radon detection system [14, 15]. Around the same collection points, in situ measurements of ^{222}Rn in soil gas were carried out. Figure 1 shows the distribution of the sampling locations across the study area. Soil samples were collected at a depth of 0 to ~ 10 cm [16], packed separately and taken to the laboratory. At the laboratory, the soil samples were initially air-dried and then oven-dried at 110 °C until a constant mass is achieved. Afterward, samples were sieved with a 2-mm mesh coupled with a sieve shaker to obtain homogenous samples of which 200 g each were then measured into a 8 cm × 7 cm cylindrical containers. The containers were thereafter sealed hermetically with adhesive tape and stored for more than 30 days so as to achieve secular equilibrium. Groundwater samples were collected from different groundwater sources. Those collected for gamma spectrometry were sealed and stored in Marinelli beaker (0.5 L) for upward of 30 days, while those collected for radon-in-water measurements were analyzed at the point of collections using a 250-mL sample vial. In order to determine activity concentration of ^{222}Rn in soil gas, soil gas samples were collected and measured in situ at the same site where groundwater and soil samples were collected. The collection of soil gas sample was carried out with RAD7 coupled with a 1.2-m-long soil gas probe manufactured by AMS Inc. The RAD7 radon gas monitor was operated in GRAB mode—a mode which allows for soil gas sample of 0.7 L to be sucked into the sample cell of the detector [17].

2.2 Measurement of activity concentration of ^{226}Ra

Soil and groundwater samples obtained in the study area were analyzed for ^{226}Ra using thalium-activated sodium iodide (NaI(Tl)) scintillation detector manufactured by Bicron [18]. The detector is coupled to a CANBERRA multichannel analyzer. The detector is housed in a cylindrical lead shield of ~ 5 cm thickness. The lead shield which shields the detector from external background radiation has a fixed base and a slidable top cover. The spectral analysis was carried out using Genie 2000 gamma analysis software. The energy calibration of the spectrometer was done using gamma sources (^{241}Am, ^{137}Cs and ^{60}Co). The standard sample used for efficiency calibration is mixed sediment obtained from International Atomic Energy Agency (IAEA), Vienna, Austria. Resolution of the detector is about 8% at 0.662 MeV of ^{137}Cs. In order to reduce statistical uncertainty, each soil sample was counted for 10 h [19]. Determination of environment background count in the laboratory was carried out by counting empty sample container which has the same geometry as the ones containing soil and groundwater samples. The background count was subtracted from the measured sample count to obtain the net count due to the radionuclides. Since radioactive equilibrium has been reached by ^{226}Ra with its decay products, its activity was determined from the gamma energy of 1764 keV of ^{214}Bi.

2.3 Measurement of activity concentration of ^{222}Rn in groundwater

Activity concentration of radon in groundwater samples was determined using RAD H_2O 250-mL bubbling kit connected in closed loop with the RAD7 radon detector. The bubbling kit comprises 250-mL glass vial, check valve, vinyl tubing, flow adaptor cap, 40-mL tygon coupler, glass frit, desiccant, vinyl tubes and retort stand. The experimental setup is shown in Fig. 2. Before the beginning of the measurement,

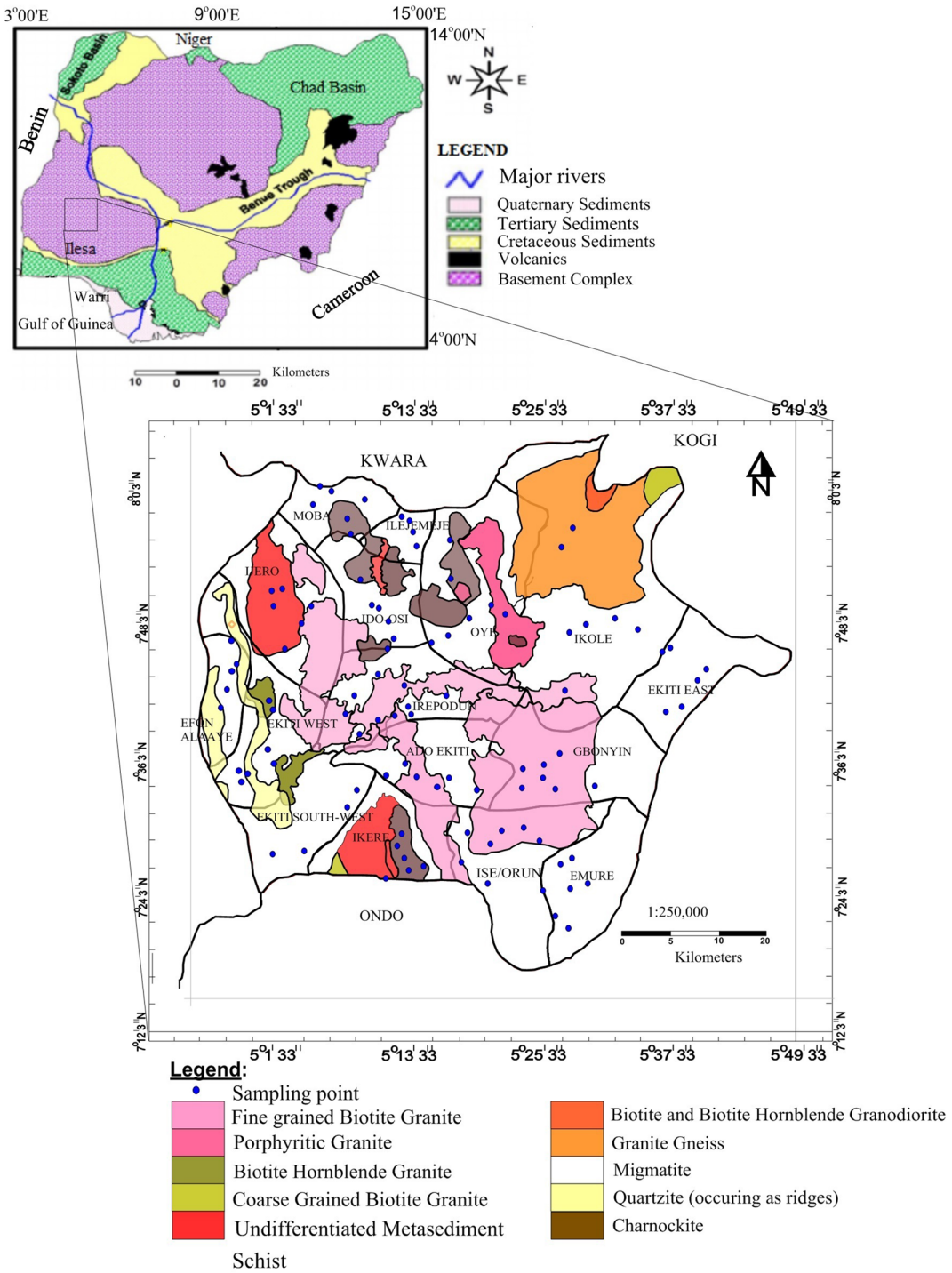

Fig. 1 Geological map of the study area showing the lithological units and sampling locations within the basement complex (inset is the geological map of Nigeria showing the basement complex and sedimentary regions. Modified from [10, 11]

the RAD7 was purged of any traces of radon using the PURGE mode. The mode allows fresh dry air to be pumped through the sample volume of the detector. The airflow during PURGE mode which passes through a laboratory drying unit ($CaSO_4$) lowers the relative humidity. The purging is continued until the relative humidity drops to 6% or lower. The RAD7 which is equipped with an inbuilt pump was operated in WAT-250 protocol. This protocol operates such that the pump aerates the water sample for a five-minute period, thereby delivering the radon gas in the water sample to the sample cell of the detector. Thereafter, the system rests for another period of five minutes to allow for radioactive

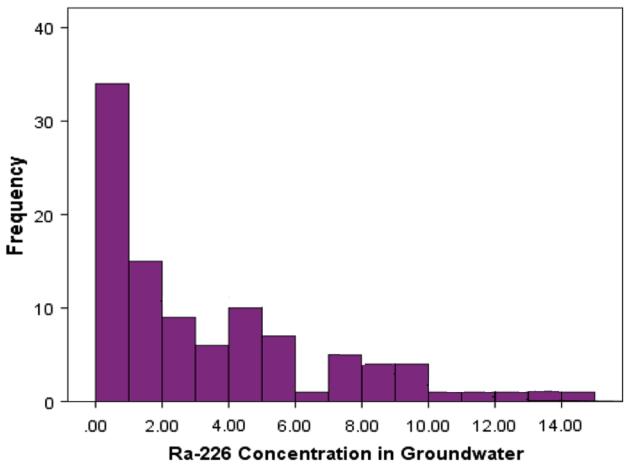

Fig. 2 Frequency distribution of activity concentrations of ^{226}Ra (Bq L^{-1}) in groundwater samples in the study area

equilibrium between Polonium-218 ($t_{1/2}$ = 3.04 min) and Radon-222. A four 5-min cycle counting commences automatically after the first ten minutes and mean value computed. The mean value of the radon content of water as at time of analysis is thereafter displayed on a readout. This value takes into account the calibration of the system, the total volume of the closed air loop and the size of the sample vial (250 mL in this case).

2.4 Measurement of activity concentration of ^{222}Rn in soil gas

The activity concentration of ^{222}Rn in soil gas was measured by employing a RAD7 radon detector with an AMS soil gas probe. The RAD7 was set to 'SNIFF' protocol which enables the detector to distinguish between 'old radon' and 'new radon' if the RAD7 had been used for a previous measurement. The sniffing process usually continues until the count rate in a dedicated window (Window A) of the detector meant for new radon activity count dropped below 0.5 cpm (count per minute). Typically, 0.5 cpm is equivalent to 40 Bq m^{-3}. To create a thoroughfare for the AMS probe into the soil, a 25-mm pilot rod was hammered down the soil to a depth of 1 m. The pilot rod was thereafter removed, and the AMS soil gas probe was inserted into the created hole while avoiding contamination of the soil gas with surface air. The soil gas probe was connected to the inlet of the RAD7 through the supplied vacuum gauge and vinyl tubes. Radon content of the soil gas was measured using a GRAB protocol which enables the extraction of soil gas into the sample cell of the detector. Radon activity concentration was then determined from a four 5-min cycle measurements similar to radon-in-water measurement.

2.5 Estimation of radiological hazards in soil and groundwater

The annual effective dose (AEDE) due to ingestion of ^{226}Ra or ^{222}Rn in groundwater depends on the water consumption rate. It is estimated using Eq. 4 [4]:

$$AEDE_{Ing,W} = A \times CR_W \times DCF$$

where A is the activity concentration of radionuclide in Bq L^{-1}, CR_W is the groundwater consumption rate in L $year^{-1}$ which is taken as 730 L $year^{-1}$ (or 2 L $days^{-1}$) for adult [13], and DCF is the dose conversion factor, 2.8×10^{-4} mSv Bq^{-1} and 3.5×10^{-6} mSv Bq^{-1} for ^{226}Ra and ^{222}Rn, respectively.

3 Results and discussion

3.1 Activity concentrations of radionuclides in groundwater and radiation dose

The summary of activity concentration values for ^{226}Ra and ^{222}Rn in 100 groundwater samples obtained across the study area and the estimated annual effective dose equivalent values due to the ingestion of the radionuclides are presented in Table 1. The activity concentration values for ^{226}Ra vary from below detectable limit (BDL) to 14.3 Bq L^{-1} with median and mean values of 3.4 Bq L^{-1} and 4.1 ± 3.4 Bq L^{-1}, respectively. 20% of groundwater samples exhibit activity concentrations which are below the detection limit of the NaI detector. 66% of the assayed groundwater samples have activity concentrations exceeding the maximum permissible level of 1.0 Bq L^{-1} set by WHO for ^{226}Ra in drinking water [20]. The frequency distribution of the activity concentrations of ^{226}Ra in groundwater samples is presented in Fig. 2 showing that the distribution is highly skewed. As seen from the figure, more of the activity concentration values fall below the mean value. The activity of ^{222}Rn in groundwater samples obtained from the study area varies from 0.9 to 472.0 Bq L^{-1} with a mean of 34.7 ± 55.5 Bq L^{-1}. 5% of the groundwater samples have activity concentrations in excess of the WHO maximum permissible level of 100 Bq L^{-1} for ^{222}Rn in drinking water [20]. The estimated annual effective dose equivalent (AEDE) values due to ingestion of ^{226}Ra in groundwater range from 0.005 to 2.917 mSv $year^{-1}$ with mean value of 0.668 ± 0.702 mSv $year^{-1}$. For ^{222}Rn, the AEDE values range from 0.002 to 1.206 mSv $year^{-1}$ with mean value of 0.089 ± 0.141 mSv $year^{-1}$. The average values are below the maximum permissible level of 1 mSv $year^{-1}$ set by the WHO [20].

3.2 Activity concentrations of radionuclides in soil

The activity concentrations data distribution characteristics of ^{226}Ra (minimum, median, maximum, arithmetic mean, standard deviation, geometric mean, coefficient of variation, skewness and kurtosis) in 100 soil samples obtained from different locations within Ekiti State are presented in Table 2. The activity concentration values range from BDL to 107.5 Bq kg^{-1} with geometric and arithmetic means of 19.0 ± 22.1 Bq kg^{-1} and 24.2 ± 18.9 Bq kg^{-1}, respectively. Although the average activity concentration of ^{226}Ra in the soil samples is below the world average value of 35 Bq kg^{-1} [7], 28% of the soil samples exhibit activities in excess of the world average value. The distribution of ^{226}Ra activity in the soil of the study area exhibits wide dispersion from the mean with a standard deviation of 18.9 Bq kg^{-1}. The distribution is highly positively skewed (+ 1.25), indicating that majority of the data are less than the mean value. However, the kurtosis value for the distribution is 2.64. This indicates the existence of more values at the extreme end of the probability curve. The coefficient of variation for the activity concentrations of ^{226}Ra is 78.2% indicating the wide spread of the values about the average value.

The in situ activity concentration measurement of ^{222}Rn in soil in the area shows that the range of activity concentration of ^{222}Rn is 6.4–298.1 kBq m^{-3} with an average value of 44.9 ± 43.9 kBq m^{-3}. The distribution of activity concentration of radon in soil is positively skewed and exhibits positive kurtosis. Generally, the distribution of activity concentrations of radon in soil in the area exhibits wide variability as portrayed by its high standard deviation value (Table 2). This is attributable to the lithology of the area as obtained experimentally by Adepelumi et al. [9] and also the permeability of the soil. The radon potential map for the study area indicating radon-prone areas (generally with $C > 30$ kBq m^{-3}) is shown in Fig. 3. As can be seen from the figure, the areas within the radon-prone areas include Otun in the northwestern part of the study area, central areas including Ido-Ekiti, Iworoko and Ado-Ekiti and Ise-Ekiti which lie in the southeastern part of the study area. These areas lie in the fine-grained biotite granite lithology of the study area. The northeastern part of the state having soil radon activity concentration between 30 and 60 kBq m^{-3} also lies in the radon-prone area of the study area. This area also lies in the granite gneiss lithology of the study area. Comparison of the radon potential map with the geological map of the study area (Fig. 1) shows that the radon-prone areas lie on the granitic lithology of the study area. Granitic rocks are typically rich in ^{226}Ra which is a parent radionuclide to ^{222}Rn.

3.3 Correlation between ^{226}Ra and ^{222}Rn in groundwater and soil

The Pearson correlation coefficient values obtained between ^{226}Ra and ^{222}Rn in groundwater and soil gas are shown in Figs. 4a–f. Correlation of ^{226}Ra and ^{222}Rn in groundwater produced insignificant correlation coefficient value of $r = -0.089$. This reveals that ^{226}Ra content of the water did not significantly contribute to the radon activity concentration of the groundwater. It further suggests that most of the radon activity concentration might have been contributed by radon produced from uranium-bearing rocks within the aquifers. Determination of Pearson correlation coefficient for ^{226}Ra and ^{222}Rn in soil shows a r value of 0.084. This value reveals a very weak relationship between the ^{222}Rn activity concentration at a depth of 1 m in the soil and ^{226}R activity concentration with 10 cm from the surface soil. This weak relationship may be attributed to the difference in sampling depth. The activity concentrations of ^{222}Rn and its parent radionuclide ^{226}Ra in the two media generally exhibit weak relationship.

Table 1 Descriptive statistics of activity concentrations of ^{226}Ra and ^{222}Rn in groundwater samples and annual effective dose

Statistic	A_{Ra} (Bq L^{-1})	AEDE$_{Ra}$ (mSv year^{-1})	A_{Rn} (Bq L^{-1})	AEDE$_{Rn}$ (mSv year^{-1})
Min	BDL	0.005	0.9	0.002
Med	3.4	0.424	18.6	0.048
Max	14.3	2.917	472.0	1.206
Arith mean	4.1	0.668	34.7	0.089
WHO Guidance Level [20]	1.0	1.000	100.0	1.000
SD	3.4	0.702	55.2	0.141
Geo. mean	2.5	0.202	19.6	0.050
Coeff. of var. (%)	82.9	1.051	1.6	1.584
Kurtosis	0.4	0.770	39.7	39.674
Skewness	1.0	1.167	5.6	5.550

Table 2 A summary of the activity concentrations of ^{226}Ra and ^{222}Rn in soil ($n = 100$)

Statistic	A_{Ra} (Bq kg^{-1})	A_{Rn} (kBq m^{-3})
Minimum	BDL	6.4
Median	19.4	32.4
Maximum	107.5	298.1
Arith mean	24.2	44.9
World Average [7]	35	–
SD	18.9	43.9
Geo. mean	19.0	33.5
Coeff. of var. (%)	78.2	97.8
Kurtosis	2.64	14.3
Skewness	1.25	3.3

4 Conclusion

This study assessed the distribution of ^{226}Ra and ^{222}Rn in groundwater and soil of Ekiti, Southwest Nigeria. The activity concentrations of the radionuclides in groundwater were found to be within the recommended threshold of the WHO [20], and the groundwater in the environment is therefore safe for consumption and other domestic uses. Radiation dose to the public due to the presence of the radionuclides in soil is also within maximum permissible level. There is a weak correlation between ^{226}Ra and ^{222}Rn in the environmental media which suggests the influence of radionuclide exchange between the media. The distribution of the radionuclides which have been mapped in this study will provide baseline information for future studies.

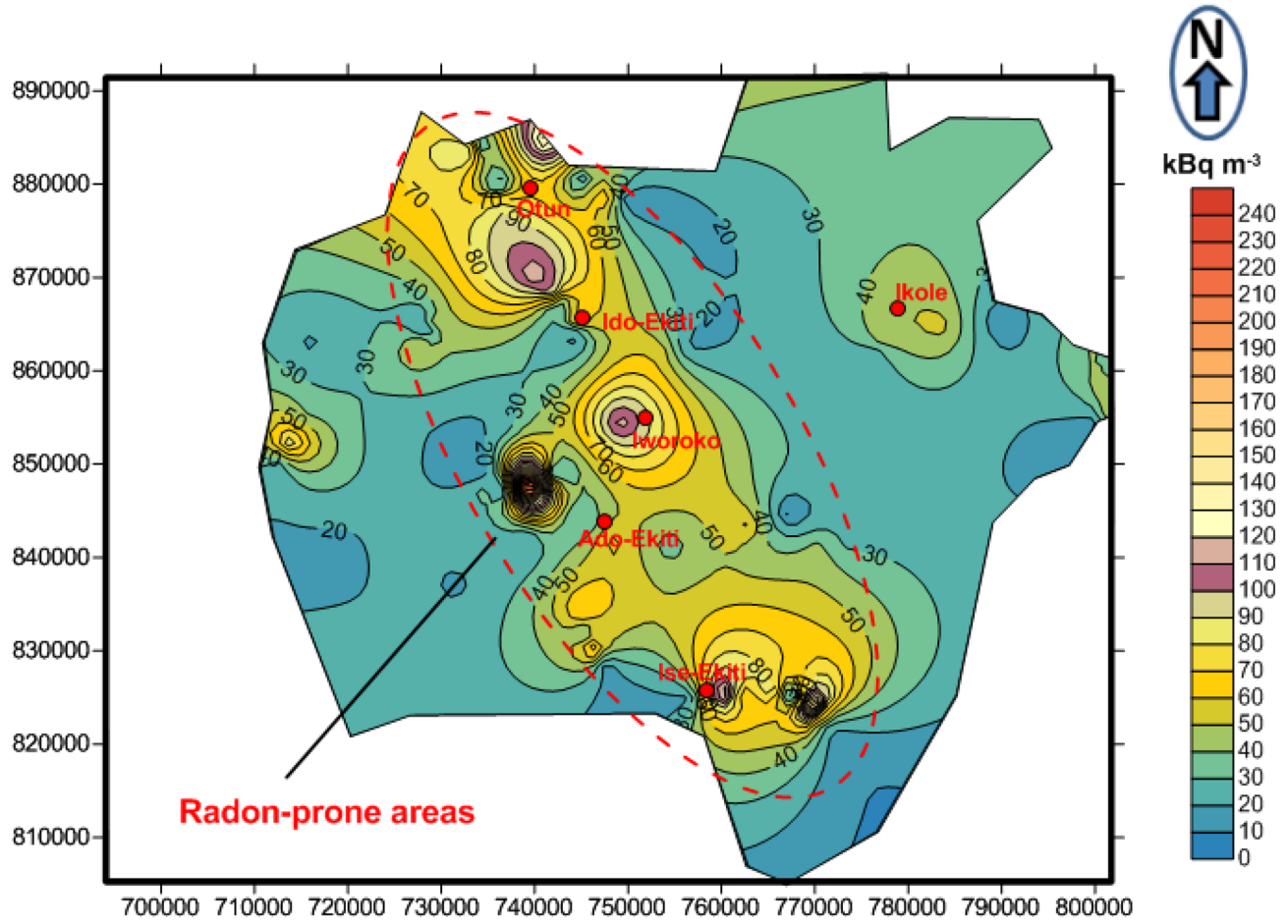

Fig. 3 Radon distribution map of the study area showing radon-prone areas

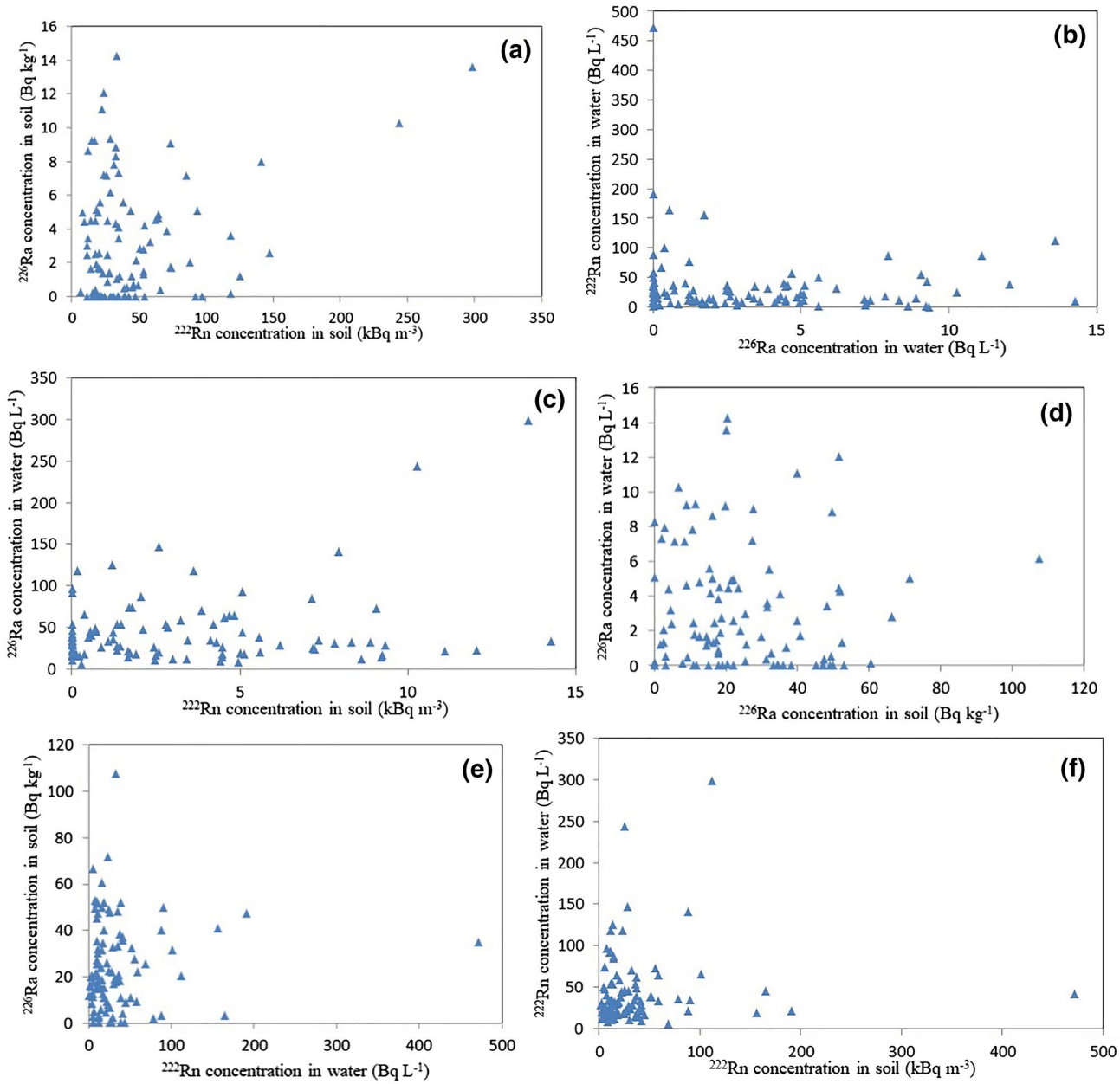

Fig. 4 Correlation plot of ^{226}Ra and ^{222}Rn activity concentrations in soil

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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