Int. J. Environ. Sci. Technol. (2018) 15:1967–1982
https://doi.org/10.1007/s13762-017-1574-x

ORIGINAL PAPER

Estimation of radiation exposure in soils and organic (animal) and inorganic (chemical) fertilizers using active technique

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Received: 4 January 2017 / Revised: 31 July 2017 / Accepted: 18 September 2017 / Published online: 25 September 2017

Abstract In this study, activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in fertilized soil samples and different organic and inorganic fertilizers used in agricultural soil were analysed using gamma-ray spectrometry NaI (Tl) detector in order to access the implications of extended use of fertilizers in 2–3 years. The concentrations of radionuclides in some granular fertilizer brands were discovered to be higher for ^{40}K, ^{226}Ra and ^{232}Th than those obtained in leafy fertilizer, animal fertilizer and fertilized soil samples. From the results, the highest overall mean concentrations of the specific activities of ^{40}K, ^{226}Ra and ^{232}Th were 2301.8 (granular fertilizer), 42.5 (leafy fertilizer) and 327.1 (animal fertilizer) in Bq kg^{-1}, while the lowest values observed in the specific activities of the same radionuclides were 357.7 (leafy fertilizer), 28.1 (animal fertilizer) and 36.5 (animal fertilizer). The radiological hazards of the radium equivalent (Ra$_{eq}$), normative value (NRN), outdoor radium equivalent (Ra$_{eq\text{-}out}$), external hazard index (H_{ext}), internal hazard index (H_{in}), dose rate, annual effective dose rate, activity utilization index and concentration accumulation index (CAI) and Ra$_{FZ}$ due to the presence of these radionuclides in the investigated samples were calculated. Nevertheless, some of the fertilizer brands have higher concentration values than the recommended limit, and the values of hazard indices of fertilizer brands used in the selected teaching and research farms were within acceptable limit. Therefore, the fertilized soil samples in the studied farms are safe.

Keywords Farms · Gamma-ray spectrometry · Hazard index · Radionuclides · Statistical methods

Introduction

Radiological hazard in phosphate rocks could be significant due to the elevated radioactivity contents of naturally occurring radioactive materials (NORMs) such as ^{40}K, ^{238}U and ^{232}Th and their progenies in some phosphate deposits (Ashraf and AL-Sewaidan 2008). Phosphate rock contains the mineral phosphorus, an ingredient used in some fertilizers to help plants grow strong roots (USEPA 2016).

Phosphorus is one of the major factors limiting plant growth in highly weathered tropical regions (Rajani et al. 1996). Soils in tropical regions, most especially Northern part of Nigeria, have low fecundity as a result of high phosphate adsorption. Moreover, fixed and adsorbed phosphorus on the surface is normally washed away by flooding and erosion; therefore, phosphorus deficiency is a major constraint to crops cultivation.

For the past 6 decades, the applications of plant nutrients such as organic and inorganic fertilizers have

Editorial responsibility: M. Abbaspour.

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increased rapidly (Ashraf and AL-Sewaidan 2008) due to high rate of food consumption in the world. Therefore, farmers are advised to cultivate crops with fertilizers (both organic and inorganic) which are essential components of agricultural practices. Over 30 million metric tons of phosphate fertilizers are annually used worldwide to increase crop production and for land reclamation (Lambart et al. 2007; Shen et al. 2010). Consequently, inorganic fertilizers affect the production quality of soil (Acton and Gregorich 1995).

Appropriate fertilizer application is an important management practice to improve soil fertility and quality. One of the sources of radioactivity other than those of natural origin is mainly due to extensive use of fertilizers (Milica et al. 2016). However, some possible negative and adverse effects of fertilizers in the contamination of cultivated lands by synthetic calcium, magnesium and nitrogen fertilizers may occur due to unwholesome practices of manufacturers. Manufacturers and legends do not inform farmers that these products undergo chemical reactions in the soil, with attendant serious side effects on the environment, soils, water, air and soil life (Heide 2007; Santos et al. 1995). Examples of the most common nitrogen and other fertilizers are $(NH_4)_2SO_4$ (21-0-0 + 24% sulphur), ammonium nitrate NH_4NO_3 (34-0-0), urea NH_2CONH_2 (46-0-0), sulphur-coated urea (46-0-0 + S), urea formaldehyde (46-0-0 + CH_2O) and dolomite lime ($CaMg(CO_3)_2$, potassium chloride (0-0-60) and triple superphosphate (0-46-0). The side effects include, but not limited to, the following; sulphur in soil reacts with water to produce sulphuric acid (H_2SO_4). In soil with excess calcium, sulphuric acid reacts with calcium carbonate ($CaCO_3$) to form gypsum which in anaerobic conditions forms H_2S with water (Casiday and Frey 1998; MAFRI 2016). The nitrates are consumed by soil organism, leached or converted to nitrogen gas and volatized. The higher the percentage of ammonium (urea) in fertilizer, greater is the acidification potential in soil (Alsaffar et al. 2016). The urea is consumed by bacteria which convert it to anhydrous ammonia and carbon dioxide ($2(NH_3) + CO_2$). Anhydrous ammonia is highly toxic and kills organisms (Salg 2016). The ammonia gas reacts with water (H_2O) to produce ammonium hydroxide (NH_4OH) with pH of 11.6. This is highly caustic and kills seeds, seedlings and soil dwelling organisms it comes in contact with. Excess magnesium in the soil can lead to a calcium deficiency in plants, since plants absorb calcium, magnesium and potassium largely in the ratio in which they are present in soil. Depending on the production process, radioactive substances and heavy metals can be extracted into fertilizers. The high concentration of radioactive ^{210}Pb in tobacco is associated with the use of acid-extracted phosphate fertilizers (Martin 2006; Mercola 2014). When processing phosphate rock to make fertilizer, the phosphorus is removed by dissolving the rock in an acidic solution. According to Saueia and Mazzilli (2006), fertilizers are formed by reacting sulphuric acid with phosphate rock, according to these reactions:

$$0.7Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3.5H_2O \rightarrow 4.2H_3PO_4 + 7CaSO_4 \cdot 1/2H_2O + 1.4HF$$

$$0.3Ca_{10}(PO_4)_6F_2 + 4.2H_3PO_4 + 3H_2O \rightarrow 3Ca\ (H_2PO_4)_2 \cdot H_2O + 0.6HF.$$

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 6.5H_2O \rightarrow 3Ca(H_2PO_4)_2{\cdot}H_2O + 7CaSO_4 \cdot 1/2H_2O + 2HF\ \text{(for Single Superphosphate SSP).}$$

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10Ca(H_2PO_4)_2{\cdot}H_2O + 2HF\ \text{(for Triple Superphosphate TSP).}$$

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4\ \text{(Monoammonium Phosphate MAP)}$$

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4\ \text{(Diammonium Phosphate DAP)}$$

Some of these fertilizers that are available in Nigeria are part of fertilizers analysed. The waste left behind after production is called phosphogypsum, which emits radon to land, air, plants and water bodies if not properly stored in stack (Skorovarov et al. 1988; Santos et al. 1995; USEPA 2016). Consequential effects of storing phosphogypsum show that in future, this method of storage might no longer be acceptable because phosphogypsum has a higher concentration of NORMs (Rutherford et al. 1994). Uranium in it decays to radium and radium decay to radon (^{222}Rn and ^{220}Rn of lifetimes 3.8d and 55.5s) a radioactive gas. Lung cancer, skin cancer and kidney diseases are health effects attributed to inhalation of radon decay products (Kumar et al. 1986). Moreover, it has been revealed that soil available nutrients coming from mineralization and available components of fertilizer absorbed by plants may lead to excessive accumulation of dose in different organs of human bodies and animals when such plants are ingested or are direct contact with dust from fertilizers (Scholten and Timmermans 1996). Agricultural usage of fertilizer could be a potential source of external and internal exposure to the farmers, warehouse keepers and general public. Therefore, the uses of fertilizers for cultivation become debatable (Ashraf and AL-Sewaidan 2008; Scholten and Timmermans 1996).

In Nigeria, information on the radioactive contents of fertilizers is scanty and not readily available. Therefore, it is essential to study the concentration of technologically enhanced naturally occurring radioactive materials (TENORM) in products such as fertilizers and to evaluate their radiological impacts on the populace.

The aim of this paper is to access (i) radioactivity contents of some commercially available fertilizers in Nigeria, because high radioactive contents may lead to a significant exposure of miners, manufacturers and end users; (ii) to estimate their radiological impact due to long-term exposure from their applications; (iii) to put forward suggestion on how to improve soil fertility using organic or inorganic fertilizers; (iv) to examine if there is an increase in soil radioactivity due to fertilizers, which may eventually lead to increase in radionuclides concentrations in various food crops. The research work was carried out from September 2014 to September 2016.

Materials and methods

Samplings

The following experimental procedures were adopted. Nineteen fertilizer brands were collected from different manufacturers in the local markets in Nigeria. The brands comprised both imported and locally made fertilizers. Three samples of each brand were collected, and their average concentrations were determined after counting. Twelve of the brands were of granular form; five of the brands were of leafy form, while the remaining two were chicken fertilizer (CF) and cattle fertilizer (CD). One factor that impacts the amount of radioactivity in fertilizer is its nitrogen, phosphorus and potassium content. This is usually specified as three sequential numbers representing the %N, %P, %K as shown in Table 1. Table 1 shows each brand, manufacturers, chemical compositions and types of crops grown by each.

Gamma spectrometric analysis

Fertilizer preparation

Fertilizer samples were air-dried and then crushed. All the samples were then oven-dried at 100 °C for 24 h and meshed to pass through 0.2-mm mesh. Two hundred and fifty grams (250 g) of each homogenized sample was filled in plastic containers of 7.6 cm diameter ×7.5 cm height.

Soil collection and preparation

Soil samples were collected from Teaching and Research Farms of Ekiti State University (TRF EKSU, Long. 7°41′N and Lat. 5°13′E) (Ayodele and Oso 2014), Ado-Ekiti in Ekiti State, an agrarian State and Teaching and Research Farms of Landmark University (TRF LU, (8°25′N, 4°40′E) (Ademiluyi and Fabiyi 2015), a University known for agrarian revolution in Omu-Aran, Kwara State Nigeria where some of the fertilizers are used for cultivation as teaching aids to students as shown in Fig. 1. About three subsamples at depth 15–20 cm were mixed to make a composite sample. Three composite samples were made from each plot, ten at EKSU and fifteen plots at LU of dimension 1.5 m × 1.5 m. Samples were collected in sampling points using coring tools. These composite samples inside polythene bags were transported to the laboratory for further treatment. The average concentrations from sampling points were then calculated and recorded to represent the concentration for that particular plot. The farms were fertilized with phosphate and animal fertilizers. Ten control samples were collected from undisturbed areas (distance 2 km) in Irasa area along EKSU and along commercial farm of LU. The mobility of radionuclides in the soil and their availability to plants depend on mineralogy composition, soil texture, pH, organic matter content and cation composition of soil solution, Ca and K concentrations. The fate of radionuclides in soil is determined

Table 1 Name of products, manufacturers, local markets, chemical compositions, plants cultivated by each product

Products	Manufacturers	Local markets	Compositions	Plants
Phostofood	Du Pont France S.A	Mikky store Ado	N 14.5%, P2O5 14%, K2O 15%, MgO 0.5%, Mn 0.2%	Pot plants, grasses, cut plants, vegetables, citrus trees
Agrolyser	Cybernetic Nigeria Kaduna	Abeokuta	Ca 20.14%, Na 1.04%, Zn 0.11% Cu 0.19%, S 2.72%, Fe trace Mn trace, Bo trace, Mo trace	Tree crops
NPK 1	Golden fertilizer	Ilesha	N 20%, P 10%, K 10%	All types of crops
NPK + 2MgO[a]	Prime Gold	Similoluwa Ado	N 12%, P 12%, K 17% + 2MgO	All types of crops
Teractiv	Olam fertilizer	Abeokuta	0:15:15 +Micronutrient Zn, B	All types of crops
SSP	Olam fertilizer	Akure	P 18%	All types of crops
Urea	Takagro fertilizer	Okesha Ado	N 46%	All types of crops
NPK 2	Golden West	Ilesha	N 20%, P 10%, K 10%	All types of crops
NPK + 2MgO[b]	Olam fertilizer	Akure	N 12%, P 12%, K 17% + 2MgO	All types of crops
Ultra sol K	Prime Gold	Ilesha	N 13%, K 46%	All types of crops
NPK 3	Olam fertilizer	Akure	N 20%, P 10%, K 10%	All types of crops
NPK 4	Elephant fertilizer	Akure	N 15%, P 15%, K 15%	All types of crops
Plantzyme	Biostadt India	Mikky store Ado	Specific gravity 1–1.3, pH 5–9 N 5%, K 0.5%, P 0.01%, Mn 0.1%, organic seaweed matter 22%, Fe 0.03%	Rice, pepper, cabbage, onion
Cocoa boost	Candel Nigeria	Ilorin	N 8.3%, P2O5 32.4%, K2O 21.1%, MgO 0.69%, Fe 0.0717%, Mn 0.0358% Zn 0.0372%, B 0.0138%, Co 0.0005%, Mo 0.0005%, pH 3.2–4.2, density 1.36–1.40 g/ml at 18 °C	Cocoa, tomatoes Pepper, fruits tree crops, cereals, maize, sorghum, vegetables
Boost Xtra	Candel UK	Ilorin	N 20%, P 20%, K 20%, MgO 1.5%, Mn 0.075%, Cu 0.075%, Zn 0.075%, B 0.0315%, Co 0.0012%, Mo 0.0012% Fe 0.15%	Tomatoes, pepper, fruits, tree crops, garden plants, cereals, maize, sorghum, vegetables
Super Gro	GNLD Int Ltd	Maraba Ilorin	N 75 g, P 45 g, K 30 g, micronutrient: S 15 g, Ca 9 g	All types of crops
Agzyme	Zenith Energy	Ilesha	N 18.5%	All types of crops
Cow fertilizer	–	EKSU Farm	N 3%, P 2%, K 1%	All types of crops
Chicken fertilizer	–	LU Farm	N 9%, P 0.5%, K 0.8%, Micronutrient: Mg 2%, Ca 0.4%	All types of crops

by general sorption processes such as ion exchange, physical adsorption and co-precipitation (Cigna and Durante 2005). The physical and chemical properties of soil samples after cropping (fertilizer application) are shown in Table 2. The moisture content of the samples was removed. Individual soil was thoroughly dried at room temperature to constant weight and sun dry at 25 ± 2 °C to drain off water. The samples were also oven-dried at a temperature of 105 °C (Alan et al. 1997). The removal of moisture took care of self-absorption in each of the samples. The dried samples were pulverized into fine grains so as to increase the total emission area (Papp et al. 2002). They were then packed in 250 g by mass and sealed in gas-tight, radon-impermeable, trap-shaped hermetical plastic container whose diameter is of the same matrix with the diameter 7.6 cm of the detector head for 4 weeks before gamma counting. This is done in order to allow the in-growth of ^{238}U and ^{232}Th decay products and achievement of secular equilibrium ^{226}Ra and ^{222}Rn with their respective progenies.

Counting

The specific activities counting in both fertilizers and soil samples were performed by gamma-ray spectrometry, employing a NaI (Tl) detector directly coupled to a pre-

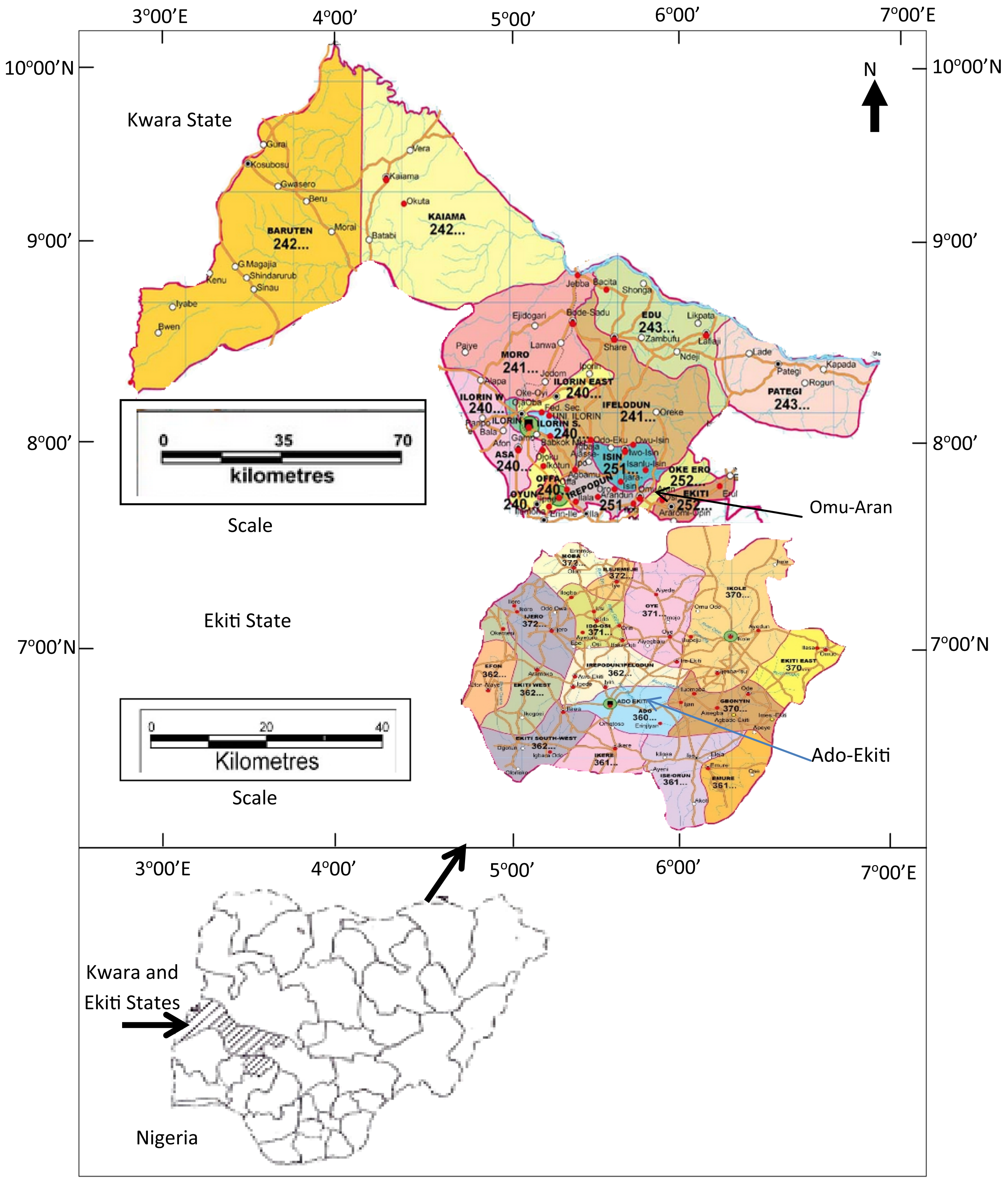


Fig. 1 Selected teaching and research farm within Ekiti and Kwara States. *Source* Nigeria Muse (2010)

Table 2 Average soil physical and chemical properties after cropping for 2–3 years

FARM (%)	pH(H2O) (%)	OM (%)	N (%)	P (mg kg^{-1})	K cmol kg^{-1}	Ca	Na	Mg	CEC	Exch acidity	Sand (%)	Silt (%)	Clay (%)	Textural	References
EKSU TRF															
7°41′N5°13′E	6.3	2.2	0.1	6	0.4	2.9	0.1	1.8	5.8	0.4	78	10	11.2	Sandy loam	(Ayodele and Oso 2014)
LU TRF															
8°25′4°40′E	6.7	4.6	0.5	6	0.1	–	–	–	–	–	–	–	–	Sandy loam	(Ademiluyi and Fabiyi 2015)

amplifier, a computer- controlled multichannel analyser (MCA). Radium content of samples was determined from intensity of 1.76 MeV energy that corresponded to the absorption of ^{214}Bi belonging to ^{238}U series that is used to identify and quantify natural uranium. Thorium content was identified by the ^{208}Tl peak which corresponded to the 2.61 MeV absorption energy. Potassium content was identified and quantified by means of the absorption of the 1.46 MeV energy that corresponded to decay of ^{40}K. Spectrum of every sample was collected for 54,000 s (15 h). To reduce the background effect, the detector was shielded with lead (Faweya et al. 2013).

Theoretical calculations

The specific activity of each radionuclide was calculated using the following equation (Singh et al. 2009) after measurement and subtraction of the background counting

$$(\text{Specific activity } A_i) = \frac{\text{CPS} \times 100 \times 100}{\text{Eff} \times \text{B.I} \times m} \pm \frac{\text{SD}_{\text{CPS}} \times 100 \times 100}{\text{Eff} \times \text{B.I} \times m}$$

where CPS is Net count rate per second, B.I is branching intensity, Eff is efficiency of the detector, m is sample mass in kg and SDcps is standard deviation of net count rate per second.

Radiation hazard parameters

In order to access the radiological hazard indices, the radium equivalent activity (Ra_{eq}, Bq kg^{-1}), outdoor radium equivalent ($\text{Ra}_{\text{eq-out}}$, Bq kg^{-1}), normative value (NRN, Bq kg^{-1}), dose rate (D, nGy h^{-1}), effective dose rates (H_{e}, mSv year^{-1}), external hazard index (H_{ext}), internal hazard index (H_{in}), gamma representative value (Iγr), activity utilization index (AUI) and concentration accumulation index (CAI) were calculated.

Radium equivalent activity (Ra_{eq})

Radium equivalent is related to the external γ-dose and internal dose due to radon and its daughters (Sahul et al. 2014). It was calculated due to the fact that high content of radionuclides in fertilizers could be crucial in the accumulation of doses in huge quantity from chemical fertilizers in various warehouses and stores. This will lead to increase in radon concentration in the surrounding air. Radium equivalent activity is calculated based on the assumption that 10 Bq kg^{-1} of ^{226}Ra, 7 Bqkg^{-1} of ^{232}Th and 130 Bq kg^{-1} of ^{40}K produce equal gamma dose. This was calculated using the following relation (UNSCEAR 2000)

$$\text{Ra}_{\text{eq}}\left(\text{Bq}\,\text{kg}^{-1}\right) = A_{\text{Ra}} + 1.43A_{\text{Th}} + 0.077A_{\text{K}} \leq 370 \qquad (2)$$

where A_{Ra}, A_{Th} and A_{K} are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, respectively.

Outdoor radium equivalent ($\text{Ra}_{\text{eq-out}}$)

The in-practice model for the calculation of Ra_{eq} was recently reviewed in the light of the UNSCEAR (2000) reported by Tufail (2012). A revised model was proposed for the determination of the Ra_{eq} for outdoor external exposure to gamma ray (Tufail 2012). Based on the revised model and the measured concentrations of the radionuclides, the outdoor radium equivalent was determined using the following relation:

$$\mathrm{Ra}_{\mathrm{eq-out}} = \left(\frac{A_{\mathrm{Ra}}}{350} + \frac{A_{\mathrm{Th}}}{270} + \frac{A_{\mathrm{K}}}{3900}\right) \times 350 \quad (3)$$

where A_{Ra}, A_{Th} and A_{K} are the activity concentrations of ^{226}Ra (in equilibrium with ^{238}U), ^{232}Th and ^{40}K, respectively.

Normative rate (NRN)

The strictest normative value for exposure to fertilizer dust during manufacturing and application on the field is referred to as normative rate NRN. In order to protect delicate organs such as liver, kidney, lung and other cancerous cells in the body, NRN value in fertilizer should not exceed 4000 Bq kg^{-1}. This index is mathematically defined as (Marina and Alexandra 2016).

$$\mathrm{NRN}\ \left(\mathrm{Bq\ kg}^{-1}\right) = A_{\mathrm{Ra}} + 1.5A_{\mathrm{Th}} \le 4000 \quad (4)$$

where NRN is the normative rate in Bq kg^{-1}, A_{Ra} and A_{Th} are the activity concentrations of ^{226}Ra and ^{232}Th, respectively.

Absorbed gamma dose rate (*D*)

The average absorbed dose rate in air is calculated. The corresponding values relative to different brands of fertilizer are calculated using the following relation (UNSCEAR 2000).

$$\mathrm{D}\left(\mathrm{n\,Gy\,hr}^{-1}\right) = A_i x C_{Fi} \quad (5)$$

where D is the dose in n Gy hr^{-1}, A_i is the activity concentration in Bq kg^{-1}, i.e. A_{Ra}, A_{Th} and A_{K} respectively, and C_{Fi} $(i = \mathrm{Ra},\ \mathrm{Th\ and\ K})$ is the dose conversion factors in units of nGy hr^{-1} per Bq kg^{-1}. The dose conversion factors as taken from UNSCEAR 2000 report based on the Monte Carlo technique are $C_{f\mathrm{Ra}}(0.462)$, $C_{f\mathrm{Th}}(0.604)$ and $C_{f\mathrm{K}}(0.0417)$ for ^{226}Ra, ^{232}Th and ^{40}K, respectively.

Annual effective dose rate (H_{E})

To estimate the annual effective dose rates for an adult person such as manufacturer, warehouses keeper and end user (farmer), the dose rates were converted to effective dose rates using the following relation (UNSCEAR 2000).

$$H_{\mathrm{E}}\left(\mathrm{mSv\ \ yr}^{-1}\right) = D\left(\mathrm{n\,Gy\,hr}^{-1}\right) \times 8760\ \mathrm{h\,yr}^{-1} \times 0.7 \times \left(\frac{10^3 mSv}{10^9}\right)\mathrm{nGy} \times 0.2 \quad (6)$$

$$= D \times 1.21 \times 10^{-3}\left(\mathrm{mSv\ \ yr}^{-1}\right) \quad (7)$$

where H_E is annual effective dose rates, D is the dose rates, 0.7 Sv Gy^{-1} is the conversion coefficient from absorbed dose in air to effective dose, 8760 is the number of hours in a year and 0.2 outdoor occupancy factor.

External hazard index (H_{ext})

A widely used hazard index reflecting external exposure is called the external hazard index H_{ext}. H_{ext} is obtained from the radium equivalent expression by assuming that its maximum value allowed which is unity corresponds to the upper limit of $\mathrm{Ra}_{\mathrm{eq}}$ (370 Bq kg^{-1}). H_{ext} is defined as follows (UNSCEAR 2000)

$$H_{\mathrm{ext}} = (A_{\mathrm{Ra}}/370) + (A_{\mathrm{Th}}/259) + (A_{\mathrm{K}}/4810) \le 1 \quad (8)$$

In addition to external hazard index H_{ext}, radon and its short-lived progenies are also hazardous to the respiratory organs of manufacturers, retailers in the stores and warehouse and end users.

The internal hazard index (H_{in})

The internal exposure to radon and its progenies is quantified by the internal hazard index H_{in} which is estimated using the following equation:

$$H_{\mathrm{in}} = A_{\mathrm{Ra}}/185 + A_{\mathrm{Th}}/259 + A_{\mathrm{K}}/4810. \quad (9)$$

Another radiation index that can be used to estimate the level of γ-radiation hazard associated with the natural radionuclide in fertilizer is gamma representative index. This is defined as

$$I_{\gamma r} = 0.0067A_{\mathrm{Ra}} + 0.01C_{\mathrm{Th}} + 0.00067A_{\mathrm{K}} \quad (10)$$

Estimated ^{226}Ra from the fertilizer. ($\mathrm{Ra}_{\mathrm{FZ}}$)

Excess ^{226}Ra which could come from fertilizer in fertilized soils is usually estimated according to the following equation (Mohannad and Khalil 2014).

$$\mathrm{Ra}_{\mathrm{fz}}\left(\mathrm{Bq\,kg}^{-1}\right) = A_{\mathrm{Ra}_s} - A_{\mathrm{Th}_s} \times \left({}^{\mathrm{U}}\!/_{\mathrm{Th}_N}\right) \times A \quad (11)$$

where A_{Ra_s} and A_{Th_s} are the activity concentration of ^{226}Ra and ^{232}Th in the fertilized soil, $\left({}^{\mathrm{U}}\!/_{\mathrm{Th}_N}\right)$ is the average value of the naturally observed $\left({}^{\mathrm{U}}\!/_{\mathrm{Th}_N}\right)$ concentration ratio 0.23, and A is a conversion factor from ^{238}U

Table 3 Activity concentration (mean ± SD, range), Raeq, Raeq-out in Bq kg^{-1}, 226Ra/232Th for radionuclides in fertilizers

Type	Product name	^{40}K	^{226}Ra	^{232}Th	Ra$_{eq}$	^{226}Ra/^{232}Th	Ra$_{eq\text{-}out}$
Granular fertilizer	Phostofood	356.7 ± 3.2	8.6 ± 1.5	184.3 ± 28.6	300	0.05	278.9
	Agrolyser	637.4 ± 4.1	19.9 ± 2.0	45.2 ± 9.9	134	0.44	135.6
	NPK 1	1337.6 ± 6.5	27.8 ± 2.3	516.6 ± 72.9	870	0.05	817.4
	NPK + 2MgO[a]	1405.9 ± 6.8	49.3 ± 3.3	533.4 ± 74.9	920	0.09	866.6
	Teractiv	10,051.5 ± 34.3	31.3 ± 2.6	1052.3 ± 143.2	2310	0.03	2295.1
	SSP	10,468.8 ± 35.7	41.5 ± 3.0	506.9 ± 70.5	1572	0.08	1637.8
	Urea	326.9 ± 3.2	37.6 ± 2.6	65.9 ± 12.7	157	0.57	152.3
	NPK 2	225.7 ± 2.9	27.5 ± 2.3	71.4 ± 13.4	147	0.39	140.0
	NPK + 2MgO[b]	921.5 ± 5.3	34.5 ± 2.6	330.1 ± 48.3	578	0.10	544.9
	Ultra Sol K	295.1 ± 3.0	12.9 ± 1.8	296.6 ± 44.0	460	0.04	424.9
	NPK 3	1187.9 ± 6.0	25.6 ± 2.3	104.1 ± 18.1	266	0.25	267.1
	NPK 4	406.2 ± 3.4	49.4 ± 3.2	217.9 ± 33.5	392	0.23	368.2
Range		225.7–10,468.8	8.6–49.4	45.2–1052.3	134–2310	0.03–0.57	135.6–2295.1
Overall mean		2301.8	30.5	327.1	676	0.20	660.72
Leafy fertilizer	Plantzyme	70.5 ± 2.2	26.2 ± 2.2	43.5 ± 9.4	94	0.61	88.9
	Cocoa Boost	500.9 ± 4.8	34.6 ± 2.6	218.0 ± 33.8	384	0.16	361.6
	Boost Xtra	300.6 ± 3.1	92.5 ± 1.3	150.8 ± 32.2	331	0.61	315.0
	Super Gro	414.0 ± 3.4	26.5 ± 2.2	54.3 ± 4.1	136	0.49	134.1
	Agzyme	592.3 ± 4.0	32.9 ± 2.5	45.5 ± 10.1	144	0.72	145.3
Range		70.5–592.3	26.2–92.5	43.5–218.0	94–384	0.16–0.72	88.9–361.6
Overall mean		357.7	42.5	102.4	218	0.5	208.9
Animal fertilizers	Cow fertilizer	802.6 ± 4.7	34.2 ± 2.6	53.9 ± 10.9	173	0.63	175.7
	Chicken fertilizer	241.1 ± 2.9	22.0 ± 2.0	19.0 ± 6.4	68	1.16	68.3
Range		241.1–802.6	22.0–34.2	19.0–53.9	68–173	0.63–1.16	68.3–175.7
Overall mean		521.9	28.1	36.5	120.5	0.9	121.9

concentration to ^{226}Ra radioactivity since 1 mg kg^{-1} of ^{238}U is equal to 12.3 Bq kg^{-1} of ^{226}Ra when the two isotopes reached secular equilibrium.

Concentration accumulation index (CAI) and activity utilization index (AUI)

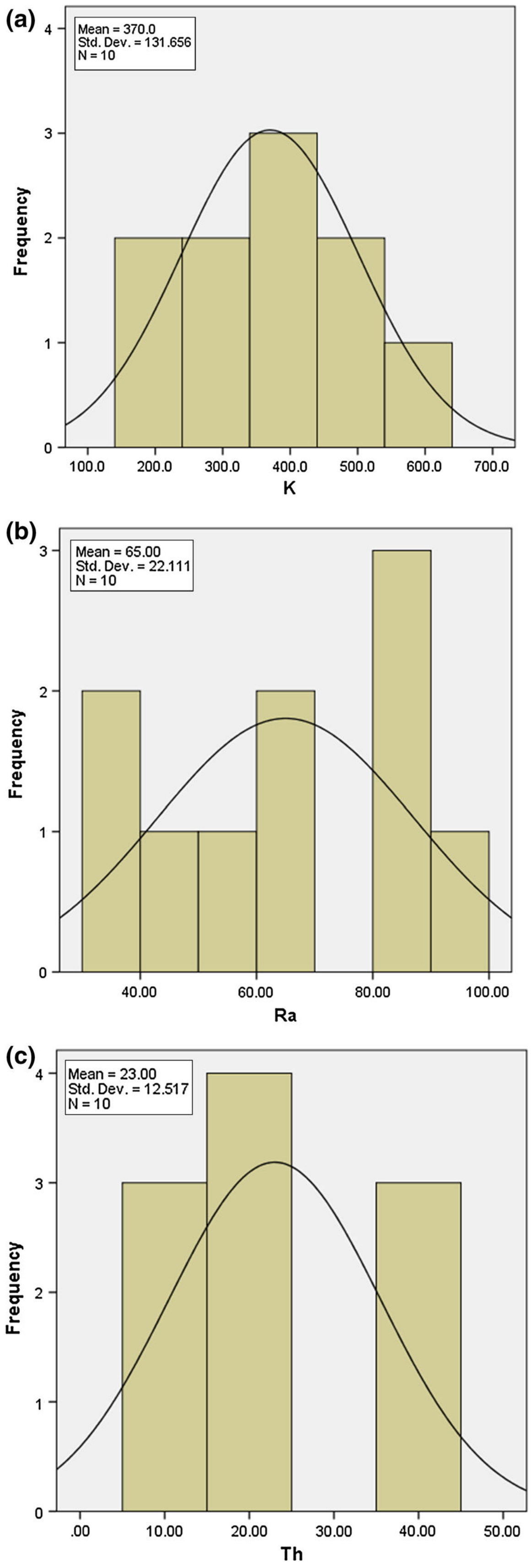
Concentration accumulation index is the direct growth of a pollutant concentration from fertilizer to soil. It is calculated after cropping (excluding concentrations in plants and those that might leach beyond the reach of crops roots) by using the concentration factor (F_c). The concentration factor expresses the ratio between the activity concentrations in soil to activity concentration in fertilizer. It is estimated using the following relation:

$$\text{CAI} = \frac{F_{\text{cfs}}}{F_{\text{cf}}} \tag{12}$$

where F_{cfs} and F_{cf} are activity concentration of fertilized soil and fertilizer, respectively.

In radiological health hazard assessment studies, activity utilization index (AUI) is usually calculated in order to estimate the dose rates in air from different combinations of the various radionuclides present in fertilizers and fertilized soils. It is given by the following expressions (Ramasamy et al. 2011)

$$\text{AUI} = \left(\frac{A\text{Ra}}{50\,\text{Bq}\,\text{kg}^{-1}}\right)F_{\text{Ra}} + \left(\frac{A\text{Th}}{50\,\text{Bq}\,\text{kg}^{-1}}\right)F_{\text{Th}} + \left(\frac{A\text{K}}{500\,\text{Bq}\,\text{kg}^{-1}}\right)F_{\text{K}} \tag{13}$$



◀**Fig. 2** **a** Frequency distribution of ^{40}K. **b** Frequency distribution of ^{226}Ra. **c** Frequency distribution of ^{232}Th

where ARa, ATh and AK are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in fertilizers and fertilized soils, respectively, $F_{\mathrm{Ra}}(0.462)$, $F_{\mathrm{Th}}(0.604)$ and $F_{\mathrm{K}}(0.041)$ are the fractional contributions to the total dose rate in air due to gamma radiation.

Results and discussion

Concentration of natural radionuclides

The mean specific activities of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1} in different brands of fertilizers and fertilized soil are given in Tables 3, 6a, b, respectively. The mean and overall mean specific activities (range) in Bq kg^{-1} of ^{226}Ra, ^{232}Th and ^{40}K in fertilizers and fertilized soils are 30.5 (8.6–49.4), 327.7 (45.2–1052.3), 2301.8 (225.7–10468.8) in granular; 42.5 (26.2–92.5), 102.4 (43.5–218.0), 357.7 (70.5–592.3) in leafy fertilizers; and 28.1 (22.0–34.2), 36.5 (19.0–53.9), 521.9 (241.1–802.6) in animal fertilizers. In fertilized soil, the mean specific activities (range) in Bq kg^{-1} of ^{226}Ra, ^{232}Th and ^{40}K are 68.2 (35.5–95.4), 27.9 (11.4–47.9), 414.9 (192.27–615.5) and 43.1 (13.6–88.6), 23.7 (5.4–51.4), 214.9 (82.7–551.8) at EKSU and LU teaching and research farms, respectively. The means of activities of control sample in Bq kg^{-1} are 53.5, 14.6, 234.9 and 43.1, 23.7, 214.9 at EKSU and LU TRFs, respectively. The highest mean concentration value of each of ^{226}Ra, ^{232}Th and ^{40}K in fertilizers in Bq kg^{-1} in Table 3 was 49.4 (NPK4), 1052.3 (Teractiv), 10468.8 (SSP) in granular; 92.5 (Boost Xtra), 150.8 (Boost Xtra), 592.3 (Agzyme) in leafy fertilizer; and 34.2 (cow fertilizer), 53.9 (cow fertilizer), 802.6 (cow fertilizer) in animal fertilizers. Table 6a, b shows that the maximum concentrations in fertilized soils were found for ^{40}K in both EKSU and LU TRFs. Figure 2 shows a comparison of the overall means of the activity concentrations in granular, leafy, animal and all fertilizer samples. It is observed that the calculated mean activity concentrations in fertilizers are higher than that of soil; therefore, all other parameters depending on concentration will follow the same trend.

Radium equivalent activity (Ra$_{\mathrm{eq}}$)

The calculated mean values of the radium equivalent activities for all types of fertilizer brands are presented in the sixth column of Table 3. The overall mean of the radium equivalent activity in granular fertilizers is at least

Table 4 Comparison of overall mean activity concentrations and radium equivalent in fertilizers in Bqkg-1 with different countries

Country	Form	^{40}K	^{226}Ra	^{232}Th	Ra$_{eq}$	References
Nigeria	Granular	2301.8	30.5	327.1	676	Present study
	Leafy fertilizer	357.7	42.5	102.4	218	Present study
	Animal fertilizer	521.9	28.1	36.5	120.5	Present study
Egypt		3	301	24	336	Hussein 1994
Egypt		4	366	66.7	462	Khalifa et al. (2005)
Finland		3200	54	11	316	Mustonen (1985)
USA		200	780	49	865	Guimond and Hardin (1989)
Germany		720	520	15	597	Pfister et al. (1976)
Pakistan		221	526	50	615	Khan et al. (1998)
Italy		4000	120	3.5	433	Righi et al. (2005)
Saudi Arabia	Granular	2059	75	23	266	Khater and Al-Sewaidan (2008)
Saudi Arabia	Leafy fertilizer	4033	–	–	311	Khater and Al-Sewaidan (2008)

threefold and sixfold higher than that of leafy fertilizers and animal fertilizers, respectively. The minimum value was calculated for chicken fertilizer, and the maximum was calculated for Teractiv and granular fertilizer. Radium equivalent activities in Bq kg^{-1} in some granular fertilizers such as NPK, (870), NPK + 2M$_g$O^a(920), Teractiv (2310), SSP (1572), NPK + 2M$_g$O^b(578), Ultra sol K (460), NPK (392) and leafy fertilizers such as Cocoa Boost (384) exceed 370 Bq kg^{-1}, the maximum permissible limit for radiation dose due to high content of ^{232}Th and ^{40}K. The overall mean radium equivalent 676 Bq kg^{-1}(granular), 218 Bq kg^{-1}(leafy fertilizers) and 120.5 Bq kg^{-1}(animal fertilizer) agreed with those obtained in fertilizer used in Egypt (Nabil et al. 2016). Uranium (^{238}U) series is more or less in equilibrium down to ^{230}Th, but ^{226}Ra and its decay products are present at much lower levels due to chemical processing of the fertilizers. Radionuclides such as ^{238}U, ^{232}Th and their decay series originate mainly from the phosphorus component of fertilizer, whereas ^{40}K originate from the potash component of the fertilizer. This indicates that the higher the level of potassium in the fertilizer, the higher the concentration of ^{40}K. Comparison of the specific activity of ^{40}K, ^{226}Ra, ^{232}Th and radium equivalent activity in Bq kg^{-1} in fertilizers from different countries is given in Table 4. The overall mean activities of ^{40}K and ^{226}Ra in Bq kg^{-1} in this study are within the range of data available in other countries such as Egypt (3)–Saudi Arabia (4033) and Finland (54)–USA (780), respectively. The overall

Table 5 Normative rates, dose rates, effective dose rates, gamma representative, external and internal hazard indices in fertilizer brands

Products	NRN(Bq kg^{-1})	D(nGy hr^{-1})	He (mSv yr^{-1})	*H*ext	*H*in	*I*γr	AUI
Phostofood	285	130.2	0.2	0.8	1.1	2.1	2.3
Agrolyser	88	63.1	0.1	0.4	0.5	1.0	0.8
NPK 1	803	380.6	0.5	2.4	3.2	6.2	6.6
NPK + 2MgO^a	849	403.6	0.5	2.5	3.3	6.6	7.0
Teractiv	1610	1069.2	1.3	6.2	7.9	17.5	13.8
SSP	802	759.5	0.9	2.2	3.0	12.4	7.4
Urea	136	71.0	0.1	0.4	0.5	1.0	1.2
NPK 2	135	65.2	0.1	0.4	0.5	1.0	1.1
NPK + 2MgO^b	530	253.8	0.3	1.6	2.1	4.2	4.4
Ultra sol K	458	197.4	0.2	1.2	1.7	3.3	3.7
NPK 3	182	124.3	0.2	0.7	0.9	2.0	1.4
NPK 4	376	171.3	0.2	1.1	1.4	2.8	3.1
Plantzyme	91	41	0.1	0.3	0.4	0.7	0.8
Cocoa Boost	362	168.5	0.2	1.0	1.4	2.7	2.9
Boost Xtra	319	146.3	0.2	0.9	1.1	2.3	2.6
Super Gro	108	51.3	0.1	0.4	0.5	1.0	0.9
Agzyme	101	67.4	0.1	0.4	0.5	1.1	0.9
Cow fertilizer	115	81.8	0.1	0.5	0.6	1.3	1.0
Chicken fertilizer	50	31.7	0.1	0.2	0.3	0.5	0.5

Table 6 Range, mean of radionuclide, Ra_{FZ} in Bqkg^{-1}, AUI and concentration accumulation index in fertilized soil and non-eroded (control) soil samples

Location	No of plots/samples		^{40}K	^{226}Ra	^{232}Th	Ra_{Fz}	$\%Ra_{Fz}$	AUI	CAI		
									^{40}K	^{226}Ra	^{232}Th
a											
Eksu TRF	10/30	1	615.5 ± 14.1	95.4 ± 4.5	41.1 ± 3.8	−20.9	−0.2	1.4			
		2	567.6 ± 18.1	85.7 ± 6.6	26.4 ± 2.5	11.0	0.1	1.2			
		3	509.7 ± 16.4	55.9 ± 7.5	47.8 ± 4.4	−79.3	−1.9	1.1			
		4	267.5 ± 8.8	42.7 ± 4.6	25.6 ± 3.3	−29.7	−0.7	0.7			
		5	335.2 ± 10.9	48.7 ± 6.1	47.9 ± 4.4	−86.8	−1.8	1.1			
		6	408.5 ± 13.2	35.5 ± 4.8	21.3 ± 2.1	−24.8	−0.7	0.6			
		7	364.1 ± 11.9	93.7 ± 7.9	21.4 ± 2.3	33.2	0.4	1.2			
		8	192.7 ± 7.7	60.7 ± 9.1	11.4 ± 1.2	28.4	0.5	0.7			
		9	433.6 ± 14.1	90.2 ± 6.9	17.6 ± 1.8	40.4	0.4	1.1			
		10	455.0 ± 14.6	73.3 ± 4.7	18.9 ± 1.8	19.8	0.3	0.9			
	Range		192.7 ± 7.7–615.5 ± 14.1	35.5 ± 4.8–95.4 ± 4.5	11.4 ± 1.2–47.9 ± 4.4						
	Mean		414.9 ± 12.9	68.2 ± 6.3	27.9 ± 2.8	11–40.4		0.6–1.4			
	Control (10)		234.9 ± 8.7	53.5 ± 7.3	14.6 ± 1.6	13.3		1.0			
Fertilizers	Urea		326.9 ± 3.2	37.6 ± 2.6	65.9 ± 12.7				1.3	1.8	0.4
NPK3			1187.9 ± 6.0	25.6 ± 2.3	104.1 ± 18.1				0.3	2.3	0.3
Cow			802.6 ± 4.7	34.2 ± 2.6	53.9 ± 10.9				0.5	2.0	0.5
b											
LU TRF	15/45	1	169.1 ± 8.5	67.0 ± 5.5	20.6 ± 8.7	8.7	0.1	0.9			
		2	137.6 ± 7.6	68.2 ± 9.6	30.1 ± 11.1	−17.0	−0.2	1.0			
		3	551.8 ± 6.5	56.3 ± 10.9	35.8 ± 7.2	−45.0	−0.8	0.9			
		4	141.0 ± 5.2	36.9 ± 6.9	29.4 ± 7.3	−46.3	−1.3	0.7			
		5	349.5 ± 4.9	35.8 ± 7.5	29.8 ± 8.5	−48.5	−1.4	0.7			
		6	205.8 ± 5.7	65.4 ± 6.2	51.4 ± 6.2	−80.0	−1.2	1.2			
		7	130.5 ± 8.6	26.1 ± 7.2	22.2 ± 8.1	−36.7	−1.4	0.5			
		8	402.3 ± 9.1	31.9 ± 6.1	14.8 ± 6.1	−9.9	−0.3	0.5			
		9	195.2 ± 8.6	13.6 ± 6.2	7.4 ± 2.7	−7.3	−0.5	0.2			
		10	224.3 ± 7.1	43.4 ± 4.2	14.4 ± 3.1	2.6	0.1	0.6			
		11	229.9 ± 8.7	23.9 ± 9.5	5.4 ± 2.6	8.6	0.4	0.3			
		12	211.5 ± 6.6	88.6 ± 8.4	34.3 ± 3.9	−5.4	−0.1	0.7			
		13	95.2 ± 9.5	32.9 ± 8.5	18.6 ± 5.4	−19.7	−0.6	0.5			
		14	82.7 ± 8.5	26.1 ± 7.2	22.8 ± 8.1	−38.4	−1.5	0.5			
		15	98.5 ± 4.6	30.7 ± 8.5	18.5 ± 9.6	−21.6	−0.7	0.5			

Table 6 continued

Location	No of plots/samples		^{40}K	^{226}Ra	^{232}Th	Ra$_{Fz}$	%Ra$_{Fz}$	AUI	CAI		
									^{40}K	^{226}Ra	^{232}Th
	Range		82.7–551.8	13.6-88.6	5.4–51.4	2.6–8.7		0.2–1.2			
	Mean		214.9 ± 7.3	43.1 ± 7.5	23.7 ± 6.6	1.3		0.6			
	Control (15)	77.63 ± 7.6	43.6 ± 5.5	13.8 ± 8.1							
Fertilizers	NPK 2	225.7 ± 2.9	27.5 ± 2.3	71.4 ± 13.4					0.9	1.6	0.3
Chicken		241.1 ± 2.9	22.0 ± 2.0	19.0 ± 6.4					0.9	1.9	1.2
Urea		326.9 ± 3.2	37.6 ± 2.6	65.9 ± 12.7					0.7	1.1	0.4

mean activities of ^{232}Th in granular (327.1) and leafy fertilizers (102.4) are higher than those available in other countries. The overall mean radium equivalent activities in granular (676 Bq kg^{-1}), leafy fertilizer (218 Bq kg^{-1} and animal fertilizer (120.5 Bq kg^{-1}) are lower than that Ra$_{eq}$ of USA (865 Bq kg^{-1}) (Khater and al-Sewaidan 2008). The present data indicate clear variations in the NOR specific activities in fertilizers from different countries but without any clear trend due to different sources of phosphate ore and chemical processing (Khater and al-Sewaidan 2008). The correlation coefficient between Ra$_{eq}$ and D is equal ($R^2 = 0.99$) from this, and the correlation between the two parameters is very good. The activity ratios of ^{226}Ra/^{232}Th in Table 3 are found to be in the ranges of 0.03–0.57, 0.16–0.72, 0.63–1.16 for granular, leafy and animal fertilizers, respectively. The fluctuations of these ratios are due to the different origins of the phosphate ores and chemical processing of the ore during fertilizers production.

Outdoor radium equivalent (Ra$_{eq\text{-}out}$)

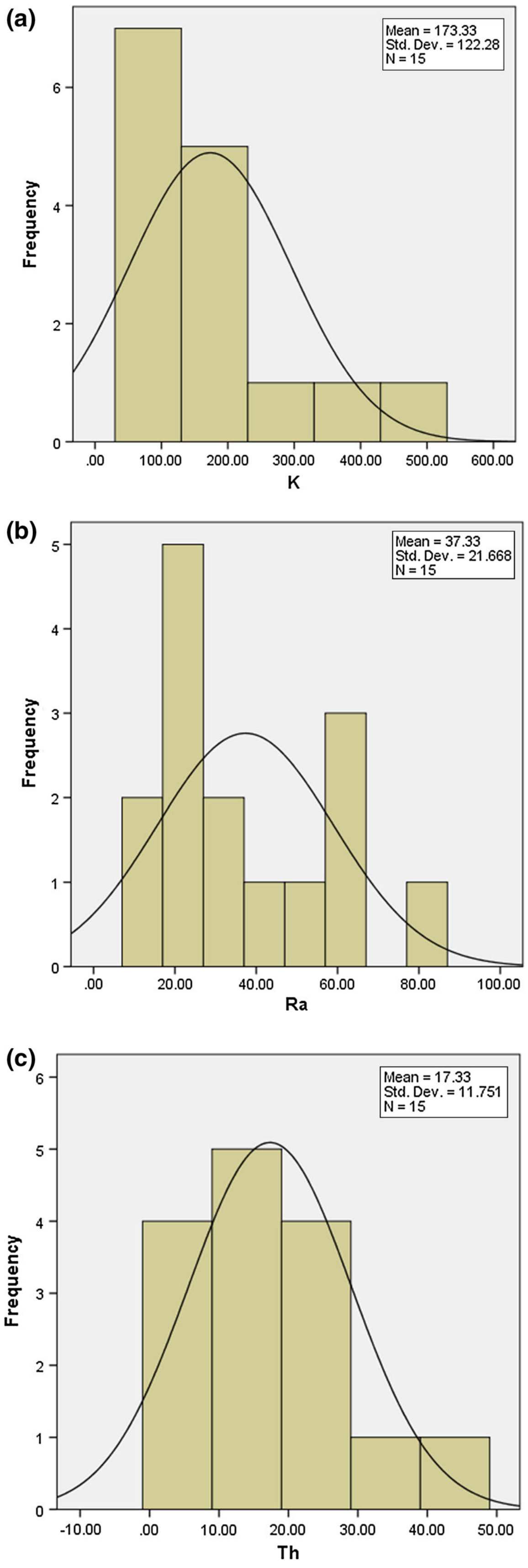
To limit the outdoor radiation from any material such as fertilizer during application to be $\leq 1\ m\,Sv\,y^{-1}$ as recommended by ICRP (1991) for the general public, Ra$_{eq-out}$ must be $\leq 350\,\text{Bq}\,\text{kg}^{-1}$. The overall means (ranges) in Bq kg^{-1} as shown in the eighth column of Table 3 for granular, leafy and animal fertilizers are 660.7(135.6–2295.1), 208.9(88.9–361.6) and 121.9(68.3–175.7), respectively. The deviations of the mean value of Ra$_{eq-out}$ of some fertilizers from the recommended $350\,\text{Bq}\,\text{kg}^{-1}$ might be due to different manufacturing processes.

Normative value (NRN)

In order to limit exposure of members of the public to harmful effects of radiation in fertilizers, a normative rate proposed by Anon (1999) was used. The normative rate (NRN) in Table 5 in Bq kg^{-1} ranged from chicken fertilizer (50) to Teractiv (1610). The highest value 1610 Bq kg^{-1} obtained in Teractiv is $< 4000\,\text{Bq}\,\text{kg}^{-1}$ proposed by Anon (1999). The correlation coefficient between NRN and D is equal ($R^2 = 0.91$) from this, and the correlation between the parameters is very good.

Dose rates (D) and annual effective dose rate (H_e)

The mean value of the gamma dose rate in air for different brands of fertilizers is presented in the third column of Table 5. From Table 5, the maximum gamma dose rate was 1069.2 $1069.2\,\text{nGyh}^{-1}$ in Teractiv fertilizer, while the



◀**Fig. 3** **a** Frequency distribution of ^{40}K. **b** Frequency distribution of ^{226}Ra. **c** Frequency distribution of ^{232}Th

minimum value found in chicken fertilizer was approximately 31.7 nGyh^{-1}. The mean annual outdoor effective dose rate of different brands of fertilizer is also given in the fourth column of Table 5 and ranges from 0.1 to 1.3 mSvy^{-1}. The estimated mean value of the annual effective dose rate of 1.3 mSvy^{-1} is a little above permissible limit in Teractiv.

Hazard indices (H_{ext}, H_{in} and $I_{\gamma r}$)

The computed values of the external, internal hazards and gamma index $\left(I_{\gamma r}\right)$ are also given in the fifth, sixth and seventh columns of Table 5. The highest values of H_{ext} and H_{in} in the studied brands are 6.2 and 7.9, respectively. The mean values of H_{ext} and H_{in} in some brands such as NPK1, NPK + 2M$_g$O^a Teractiv, SSP,NPK + 2M$_g$O^b, Ultra sol K and NPK4 are higher than the recommended value of l. The calculated $\left(I_{\gamma r}\right)$ values in some of the samples under investigation exceed the upper limit which is unity. It is clear that the $\left(I_{\gamma r}\right)$ level in fertilizers such as phostofood (2.1), Ultra sol K (3.3), NPK 3(2.0), NPK 4(2.8), Boost Xtra (2.3) and Cocoa Boost (2.7) are high, while NPK1 (6.2), NPK + 2M$_g$O^a (6.6), Teractiv (17.5), SSP (12.4), NPK + 2M$_g$O^b (4.2) are very high.

Activity utilization index (AUI) and concentration accumulation index (CAI)

The mean value of the AUI for different brands of fertilizers and fertilized soil samples is presented in the eighth column of Tables 5, 6a, b, respectively. The calculated values of the AUI in fertilizers vary from 0.5 (chicken fertilizer) to 13.8 (Teractiv) fertilizers, while it varies from 0.6 to 1.4(EKSU TRF) and 0.2–1.2 (LU TRF) in fertilized soil samples with mean 1.0 and 0.6 in both farms, respectively. These mean values in fertilized soil show that AUI <2 correspond to an annual effective dose <0.3 mSvy^{-1} (El-Gamal and Nasr 2007). This indicates that fertilized soil samples are safe. Concentration accumulation indices calculated in fertilized soils using fertilizers that are commonly used in both farm range between 0.3 and 1.3, 1.8–2.3, 0.3–0.5 and 0.5–0.9, 1.6–1.9, 0.3–1.2 of ^{40}K, ^{226}Ra, ^{232}Th in columns ninth, tenth and eleventh of Table 6a, b, respectively. The mean values are 0.7, 2.0, 0.4 and 0.8, 1.5, 0.6 as shown in Table 6a, b and are ≤ 2 that correspond to an annual effective dose <0.3 mSvy^{-1}. This indicates that annual effective dose rate is still within acceptable limit of 1 mSvy^{-1}.

Estimated ^{226}Ra from fertilizers

As shown in Table 6a, b, the Ra_{FZ} values were 11.0–40.4 with mean value of 13.3 Bq kg^{-1} and 2.6–8.7 with mean value 1.3 Bq kg^{-1} at EKSU and LU TRFs, respectively. The contributing percentage of Ra_{FZ}/total ^{226}Ra in some soil samples have negative values and percentages. This indicated that certain concentration of ^{226}Ra in the applied fertilizers in both farms must have been leached away or consumed by crops. The total mean contribution percentages are 1.7 and 0.6 in EKSU and LU TRFs, respectively. The results implied that contribution of ^{226}Ra in agricultural soils is low.

Descriptive statistics

Descriptive statistics of the mean activity concentration radionuclides in fertilized soil samples are given in Figs. 2a–c and 3a–c. The standard deviation was the greatest for ^{40}K in fertilized soil samples and was the smallest for ^{232}Th. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in this study have positive skewness values, which indicate that the distribution are asymmetric in nature. The distributions of ^{40}K in Fig. 3a and ^{226}Ra in Fig. 3b have longer tails to the right of the central maximum than the left; the distributions have positive skewness. Kurtosis is the degree of peaked of a distribution for real-valued random variable. Kurtosis characterizes the relative peaked or flatness of a distribution compared to normal distribution. Figure 3c (^{232}Th) shows a relatively high peak and exhibits leptokurtic distribution (Raghu et al. 2015); while Figs. 2a, c, 3a, b which are not very peaked or very flat-topped are mesokurtic in nature. Figure 2b shows a relatively flat-topped and called platykurtic distribution. The distributions in the present study associated with ^{40}K (Fig. 2a), ^{232}Th (Fig. 2c), ^{40}K (Fig. 3a), ^{226}Ra (Fig. 3b) and ^{232}Th (Fig. 3c) radionuclides have positive kurtosis values indicating peaked distribution and ^{226}Ra (Fig. 2b) radionuclides have negative kurtosis values indicating flat distributions. In statistics, the correlation coefficient R measures the strength and direction of linear relationship between two variables. Correlation of activity concentrations between fertilized and control soil samples was carried out. The results are 0.444, −0.304, −0.283 and 0.556, 0.715, 0.475 for, ^{40}K, ^{226}Ra and ^{232}Th at EKSU and LU, respectively. The results fluctuated between a weak downhill (negative) and a moderate uphill (positive) linear relationship for EKSU and LU, respectively. Therefore, strength of fertilizers application in soil samples at EKSU is more than that of LU.

Conclusion

Fertilizers and fertilized soil samples were measured for their radioactivity content using gamma spectrometry technique. The data revealed that the mean activity concentration in fertilized soil samples was within the world average (UNSCEAR 2000). The differences in the activity levels in fertilized and control soil samples have been observed to be lying within activity values measured all over the world. However, some fertilizers samples show much higher concentrations. Fertilized soil samples satisfied the universal standards (UNSCEAR 2000) limiting the radioactivity within safe limits of 4000, 1000 and 1000 Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th, respectively. The radium equivalent and outdoor radium equivalent in fertilizers brands such as NPK 1, NPK + $2M_gO^a$,Teractiv, SSP, NPK + $2M_gO^b$, Ultra sol K, NPK4, Cocoa Boost was higher than the recommended limits (370 and 350 Bq kg^{-1}). These wide variations in gamma activity in the aforementioned fertilizer brands could be attributed to the difference in the factories that manufactured fertilizers, difference in places where raw materials were sought and different geomorphological conditions. As far as the mutual comparison of the fertilized and control soil samples of the area under investigation is concerned, there is a slight increasing activity in fertilized soils. This is due to uranium, thorium, radium and their progenies in phosphate rocks which are essential raw materials used to manufacture different brands of fertilizers (Hussain et al. 1994; Skorovarov et al. 1996).

Based on the radionuclide results, the radiological hazards of NRN, D, H_{ext}, H_{in}, H_e, $I\gamma r$ and AUI were calculated and showed value greater in some fertilizer brands than the worldwide safety limit. These brands should be under radiation protection. Nevertheless, from the viewpoint of biological effect of radiation, the use of urea, NPK2, NPK3, cow and chicken fertilizers in EKSU and LU TRFs did not cause any effect on human health and radiological impact of such practice is negligible. Therefore, the use of organic fertilizers such as cow and chicken fertilizers should be encouraged and take pre-eminence over synthetic fertilizers.

Acknowledgements The first author acknowledges the authority of Landmark University for granting him the opportunity to spend his sabbatical leave there. Part of the fund realized during that period was used to finance the major part of the work. The authors of this article also acknowledge the following people: Miss Damilola, Mr Jegede and Miss Oguntuase Elizabeth for their assistance in field sampling and laboratory work.

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