INVESTIGATION AND EVALUATION OF RADIOLOGICAL RISK ASSOCIATED WITH NITROGENOUS FERTILIZER IN NIGERIA USING GAMMA RAY SPECTROMETER.

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ABSTRACT

Urea fertilizer is considered as the most important nitrogenous fertilizer sold in Nigerian market. The use of urea fertilizers to enhance growth of vegetable crops, flowers and lawn has recently drawn public concern in the aspect of its contribution to environmental radioactivity. Potential radiological risk due to the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer samples collected from local supplier in different locations in southwestern Nigeria was determined using NaI(Tl) gamma ray spectrometer detector. Results of analyses showed that activity concentration of ^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer ranged from 154.3±7.9 to 2907±18.8 $Bq\,kg^{-1}$; 7.5±5.2 to 23.4±10.7 $Bq\,kg^{-1}$ and 28.2±3.8 $Bq\,kg^{-1}$ respectively with total mean values of 183.6±9.6 $Bq\,kg^{-1}$, 13.2±5.8 $Bq\,kg^{-1}$ and 38.3±10.0 $Bq\,kg^{-1}$ respectively which were lower than the corresponding maximum safety limit for soil. Furthermore, estimation of absorbed dose rate in air and outdoor annual effective dose were below the standard safety limit 60 $nGy\,h^{-1}$ and 0.07 $mSv\,y^{-1}$ respectively.. External and internal hazard indices as well as alpha index were determined with results less than unity (1.0) as the standard safety limit; an indication that there is no radiation risk associated with the use of investigated urea fertilizer samples, therefore, samples investigated were radiologically safe to users of the fertilizer product.

Keywords: Urea fertilizer, natural radionuclides, ionizing radiation, gamma ray spectrometer.

INTRODUCTION

Solid waste from poultry (such as Broiler dung) goat manure, sheep manure, cow dung and are classified as organic fertilizers. While inorganic fertilizers include Nitrogen-Potassium-Phosphorus (NPKs) and Single Super Phosphate (SSP). Organic and chemical fertilizers are common brands of fertilizers in use by farmers to provide nutrient to crops, support vegetative growth of plants, improve flowering and roots development and strengthen resistance to pest attack to feed the world's rapidly increasing population. Urea is formed naturally by metabolizing protein in human as well as other mammals, amphibians and some fishes. It is also produced when ammonia reacts with carbon (IV) oxide at 150 ℃ and at a high pressure of about 150 atmospheres.

Urea fertilizer is a type of nitrogenous fertilizer, a white crystalline substance in appearance with the chemical formula NH_2CONH_2. It is the main nitrogen containing substances in the urine of mammals, neutral in pH and can adapt to almost all kinds of soil. Urea fertilizer aids photosynthesis process of plants and is highly water soluble; containing 46% of nitrogen (46N) with molar mass of 60.06 g/mol. Nitrogen is supplied mainly in the form of ammonia which in turn is obtained from fossil fuels. The ammonium compounds used as sources of nitrogen are ammonium trioxonitrate (V) and some sodium trioxonitrate (V).

Main function of urea fertilizer is to provide plants with only nitrogen (and not phosphorus and potassium), promote green leaf growth. Nitrogen support vegetative growth, phosphorus improves roots and flowering, while potassium strengthens resistance to environmental attacks from extreme temperature and as to pest attack. Nitrogen in fertilizers is in the form of ammonium (NH_4^+ cation), which is quickly transformed by bacterial in the soil to the nitrate (NO_3^- anion) depending on the soil temperature. Fertilizers enter the human food chain through plants (Alsaffar *et al.*, 2016) and edible fruits

In Ibadan, Nigeria, the local economies are characterized by agricultural activities. While organic and chemical or phosphate fertilizers are the major sources of soil fertility in the area. Phosphate is used in the production of some organic and chemical fertilizers. Phosphate has been reported to be rich in radioactive elements ^{226}Ra, ^{232}Th and ^{40}K, therefore, a major contributor to terrestrial outdoor and internal radiation doses. During buying and selling of the urea fertilizer products, customers, farmers sellers drivers and loaders in bags and trucks may be exposed to doses of ionizing radiation through internal exposure (inhalation) and external exposure (direct physical contact with hands or legs). ^{226}Ra, ^{232}Th and ^{40}K may be absorbed by plants or crops and transported to their eatable parts becoming a source of internal exposure to human cells. Some radiation sickness associated with ionizing radiations are new cases of cancer, skin burn, leukemia, skin cancer, cataract, infertility (Nwaka*et al.*, 2018; Ononugbo and Nwaka, 2017; Nwaka and Enyinna, 2016).

It is worth mentioning that some researchers have studied organic, chemical and phosphate fertilizers and taken measurements in some areas in Nigeria, Egypt, Algeria, Iraq among other countries (Hiwa*et al.*, 2020; Amina *et al.*, 2019; Hassan *et al.*, 2016; Nwaka and Jibiri 2018; Jibiri and Fasae 2013; Raad and Hayder 2011).Hiwa*et al.* (2020) established that application of chemical fertilizers elevated the natural radioactivity level of soil in Algeria. Uddin*et al.* (2017) reported that ^{226}Ra, ^{232}Th and ^{40}K in some samples of urea fertilizer samples from Chittagong Fertilizer Company Limited and Jamuna Fertilizer Company Limited exceeded the world average values. Alsaffar*et al.* (2016) found that uptake of ^{226}Ra, ^{232}Th and ^{40}K radioactive elements by rice grains was affected by different concentrations of fertilizer and its application time. Raad and Hayder (2011) published that no activity concentrations were found in urea fertilizer because the ore did not contain natural radionuclide; furthermore, ^{238}U specific activity in the local (Iraq) granular NPK6 fertilizer samples was much higher than that of the imported granular and leafy sample by Iraqi governorate. In a study carried out by Amina *et al.* (2019) in Algeria, the radiological effects of the fertilizers were found to be safe for public and environment and also under the limit of international recommended values.

Radiological risk assessment of urea fertilizer due to activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer was necessary because of serious concern that buyers, sellers, users of the urea fertilizer products, and manufacturers may be exposed to elevated doses of ionizing radiation. There is fear that urea fertilizer is radiologically unsafe for agricultural and other purposes. The objectives of the study were (i) to determine the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer and compared with acceptable safety limit. (ii) to determine the mutual relationship and strength of association between radionuclides of interest ^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer samples using regression analysis. (iii) to determine the absorbed dose (D) rate in air, and outdoor annual effective dose (E_{out}) (iv) to estimate external hazard index (H_{ext}) and internal hazard index (H_{int}), alpha index (I_{α}), so as to compare with international standard safe limit.

MATERIALS AND METHOD

Sampling and sample preparation of urea fertilizer

Ten (10) urea fertilizer samples made in Nigeria were purchased/collected from local marketers in Ibadan and transported to Radiation and Health Research Laboratory, University of Ibadan, Ibadan, Nigeria for preparation prior to gamma counting. Effort was made to ensure that urea fertilizer collected for analysis was certified by National Agency for Food Drug Administration and Control (NAFDAC). Each of the samples was dried and pulverized to fine particles, weighed (200±1g) and transferred into a cylindrical plastic container selected based on the space allocation of the detector vessel which measures 7.6cm by 7.6cm in dimension (geometry). To prevent radon – 222 (^{222}Rn) from escaping, the packaging in each case was sealed with masking adhesive tape. Radon and its short – lived progenies were allowed to reach secular radioactive equilibrium by storing the samples for thirty (30) days prior to gamma spectroscopy measurements.

Calibration of the gamma ray spectrometer detector

The spectrometer used was a 7.6cm $\times$ 7.6cm sodium iodide activated with thallium [NaI(Tl)], highly efficient detector crystal, well calibrated and lead cylindrical shielded of 10cm thickness to reduce the effects of laboratory background radiation and scattered radiation. The detector was coupled to a Canberra series 10 plus Multichannel Analyzer (MCA) through a photomultiplier tube (PMT) and amplifier. Energy calibration of the detector was carried out so as to identify the various radioactive elements of interest present in the urea samples through gamma energies they emit. A set of International Atomic Energy Agency (IAEA) standard sources of known radionuclides with well-defined energies within the range of interest was used. Details of the detector characteristics, energy calibration and detector efficiency were reported in Nwaka and Jibiri (2018). The system has a unique advantage of operating on a D.C power supply battery which can be charged. The battery can run continuously for 10 hours if there is power failure so that counting of samples will not be interrupted.

Measurement of radioactive element of interest

In order to determine the activity concentrations of radioactive elements of interest in the urea fertilizer sample in this study, relevant transition peaks were considered. The activity concentrations of ^{226}Ra and ^{232}Th were determined indirectly through the activities of their decay products. The ^{238}U (which is due to ^{226}Ra) content of the urea fertilizer samples was determined from the intensity of 1.760 MeV gamma ray peaks of ^{214}Bi, for ^{232}Th, it was determined from the intensity of the 2.615 MeV gamma ray peaks from ^{208}Ti while for ^{40}K content of the urea fertilizer samples, it was determined from 1.460 MeV gamma ray peaks emitted during the decay of ^{40}K. Fig 1 showed relationship between channel number and energy calibration of the detector which was a very strong positive relationship; therefore the detector is reliable. Background radiation of the laboratory and environ was determined by placing an empty plastic container of the same dimension as the stored samples for 30 days in the detector and counted for 10hours. Thereafter, the gross counting in detector for each urea fertilizer sample in a container was carried out for 10 hours and net count determined by subtracting the background count from the gross count. The peak area of each energy in the spectrum were used to compute the activity concentrations in each sample by the use of modified equation 1 (Nwaka and Jibiri 2018; Jibiri *et al.* 2010).

$$C\,(\mathrm{Bq\,kg^{-1}}) = \frac{C_n}{C_{fk}} \quad (1)$$

Where, C is the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in urea samples given in $\mathrm{Bq\,kg^{-1}}$, C_n is count rate (counts per second) and C_{fk} is calibration factor of the detecting system.

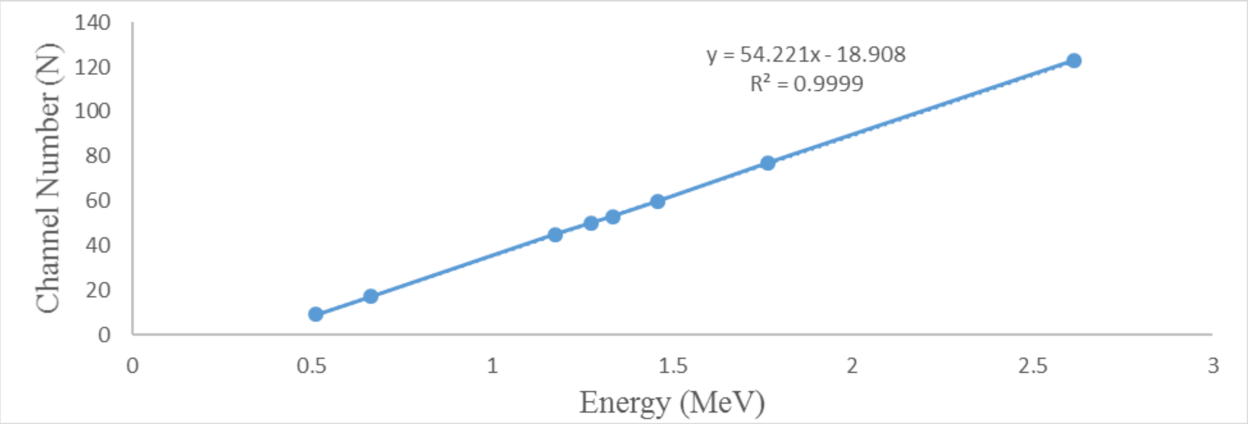

Fig 1: Channel number versus energy calibration relationship

RADIOLOGICAL INDICES DUE TO UREA FERTILIZER

Absorbed dose rate (D) in $\eta Gy\ h^{-1}$

Absorbed dose rate due to the gamma rays emitted for urea fertilizer samples was calculated from activity concentrations of radioactive element of interest ^{40}K, ^{226}Ra and ^{232}Th using (UNSCEAR 2000).

$$D(\eta\mathrm{Gy\,h^{-1}}) = 0.042\,A_K + 0.462A_{Ra} + 0.604\,A_{Th} \quad (2)$$

A_K,A_{Ra}, and A_{Th} are activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th respectively. 0.042, 0.462, and 0.604 are dose coefficients in $\eta\mathrm{Gy\,h^{-1}}$ per $\mathrm{Bq\,kg^{-1}}$ for ^{40}K, ^{226}Ra and ^{232}Th respectively.

Annual effective dose (H_E) in $mSv\ y^{-1}$

Annual effective dose was calculated from the absorbed dose rate by applying the dose conversion factor of 0.7 Sv/Gy and outdoor occupancy factor of 0.2 using (UNSCEAR 2000).

$$H_E = D(\eta\mathrm{Gy\,h^{-1}}) \times 8760h\ y^{-1} \times 0.2 \times 0.7Sv/Gy \times 10^{-6} \quad (3)$$

External hazard index (H_{ext})

External hazard index is a measure used to estimate the gamma radiation associated with the radioactive element of interest determined using equation 4 and presented in Table 1. External hazard index should be less than unity (UNSCEAR 2000).

$$H_{ext} = \frac{A_K}{4810} + \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} \leq 1 \quad (4)$$

Internal hazard index (H_{in})

Radon and its short – lived products are hazardous to respiratory organs therefore internal hazard index due to radon and its daughter was calculated using equation 5, and presented in Table 1. External hazard index should be less than unity. (UNSCEAR 2000).

$$H_{int} = \frac{A_K}{4810} + \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} \leq 1 \quad (5)$$

Alpha index (I_α)

Radiation due to the released radon from the urea fertilizer samples were calculated using alpha index represented in (UNSCEAR 2000).

$$I_\alpha = \frac{A_{Ra}}{200} \quad (6)$$

RESULTS

Results of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K radioactive element were presented in bar chart in Fig. 2.Fig. 3 showed the regression plot between ^{40}K ($Bq\ kg^{-1}$) and^{226}Ra ($Bq\ kg^{-1}$), Fig. 4 showed the regression plot between ^{40}K ($Bq\ kg^{-1}$) and^{232}Th($Bq\ kg^{-1}$), Fig. 5 showed the regression plot between^{226}Ra($Bq\ kg^{-1}$) and^{232}Th($Bq\ kg^{-1}$). Table 1 showed radiological indices due to activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer.

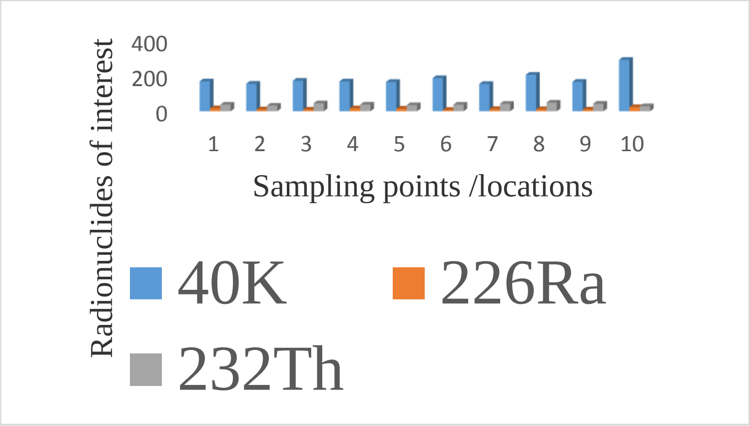

Fig 2: Bar chart showing variation of radioactive elements of interest^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer samples with different locations

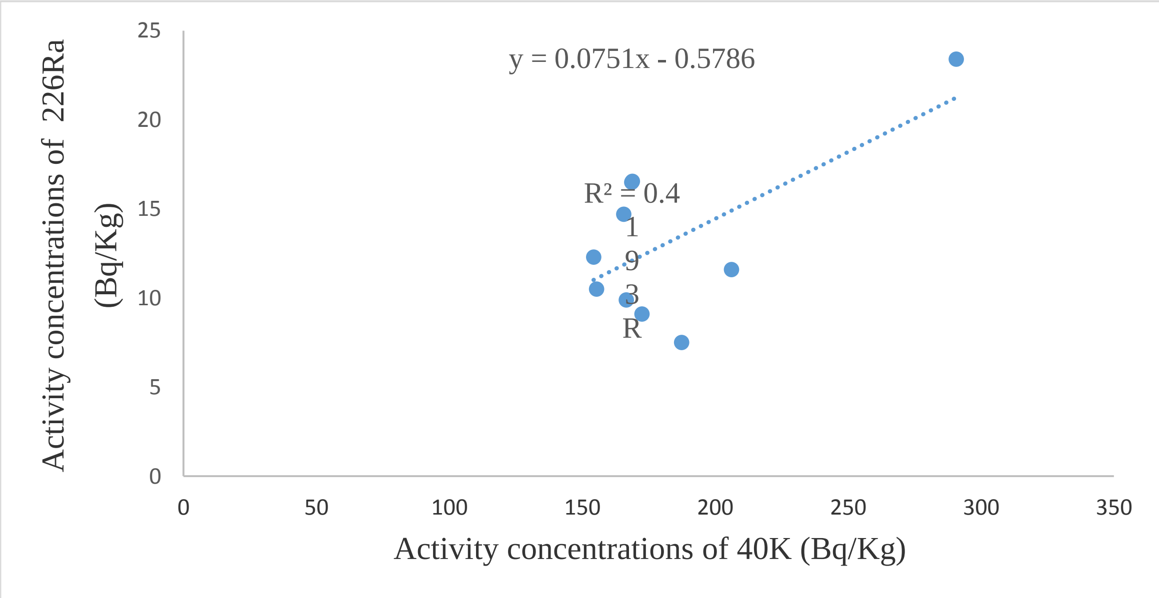

Fig. 3: Regression plot between ^{40}K ($Bq\ kg^{-1}$) and^{226}Ra ($Bq\ kg^{-1}$)

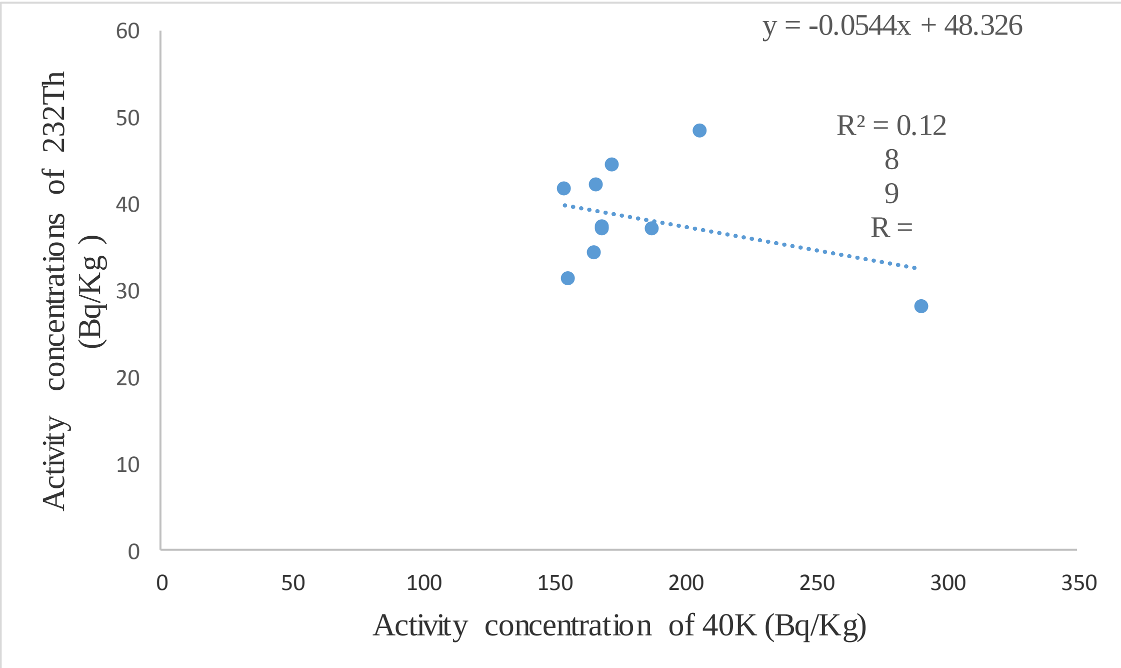

Fig. 4: Regression plot between ^{40}K ($Bq\ kg^{-1}$) and^{232} Th($Bq\ kg^{-1}$)

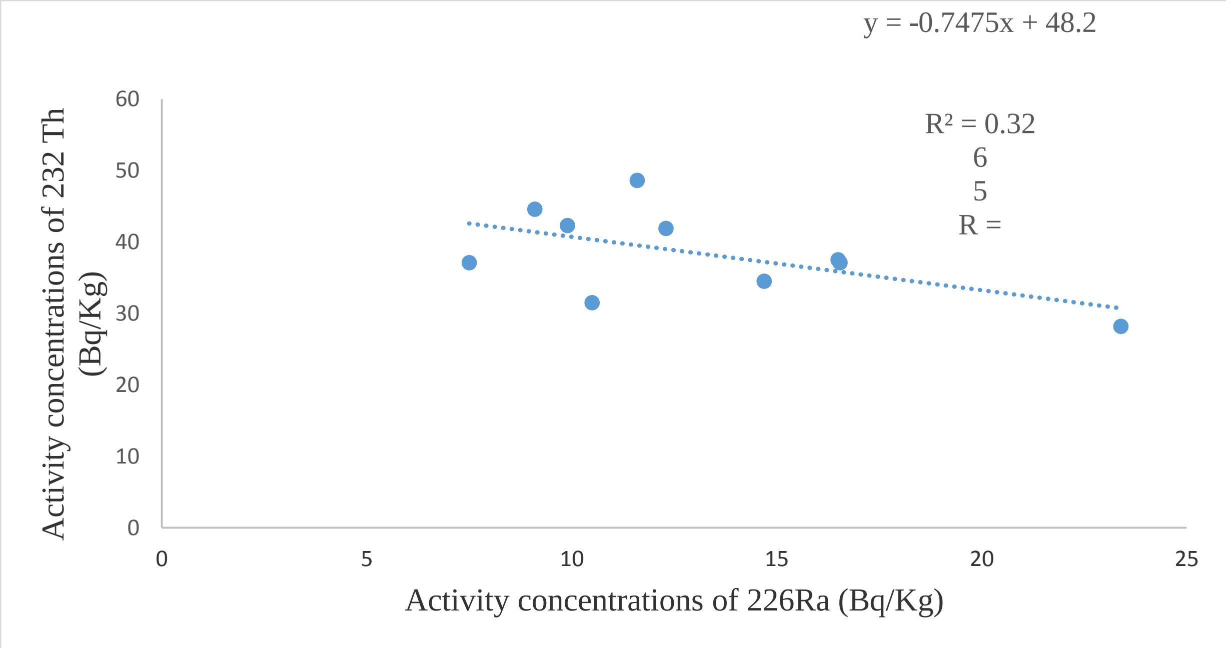

Fig. 5: Regression plot between ^{226}Ra($Bq\ kg^{-1}$) and ^{232}Th($Bq\ kg^{-1}$)

Table 1: Radiological indices due to activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in urea fertilizer

Sampling points	**Absorbed dose rate D ($nGy\ h^{-1}$)**	**Outdoor annual effective dose E ($mSv\ y^{-1}$)**	**External Hazard Index (H_{ext})**	**Internal Hazard Index (H_{int})**	$I_\alpha = \frac{A_{Ra}}{200}$
A	37.1	0.046	0.22	0.27	0.083
B	30.3	0.037	0.18	0.21	0.053
C	38.2	0.047	0.23	0.27	0.046
D	37.2	0.046	0.24	0.27	0.083
E	34.6	0.042	0.21	0.25	0.071
F	33.6	0.041	0.20	0.23	0.038
G	37.5	0.046	0.23	0.26	0.062
H	43.4	0.053	0.26	0.29	0.058
I	37.1	0.046	0.22	0.25	0.050
J	40.1	0.049	0.23	0.30	0.117

Mean	36.9	0.045	0.22	0.26	0.077
Safety limit (UNSCEAR, 2000; 2012)	60	0.07	1.0	1.0	1.0

DISCUSSION

Generally, mean activity concentrations of radionuclides ^{40}K and ^{226}Ra were lower than the safe limit 400 $Bq\ kg^{-1}$and 30 $Bq\ kg^{-1}$ whereas mean ^{232}Th activity concentrations (38 $Bq\ kg^{-1}$) exceeded the safe limit 35 $Bq\ kg^{-1}$ (Fig.1). It was also found that 30% of ^{232}Th activity concentrations were below the safety limit. Highest activity concentration as observed in Fig 1 was found in ^{40}K followed by ^{232}Th and then ^{226}Ra radioactive element; an evidence that the raw materials used for production of urea fertilizer samples investigated contain more of ^{40}K among other radioactive elements investigated. Similar result of the study recorded for ^{40}K concentration as the highest mean value than other measured parameters (^{226}Ra and ^{232}Th) were reported from agricultural fertilizers from Iraqi markets (Akram, 2021) and urea fertilizer in Iraq (Yasmyn and Kareem, 2021). This present study differed with Raad and Hayder (2011) study where no activity concentrations were found in urea fertilizer. Furthermore, activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th were found higher than urea fertilizers (D.3, D.4, D.5) used in Iraq (Nada *et al.*, 2020), however agreed with the study carried out by Uddin*et al.* (2017) where some samples of urea fertilizer in ^{232}Th exceeded the world safe limit.

As observed from Fig. 3, Fig. 4 and Fig. 5 respectively, there exist strong and positive relationship between ^{40}K and ^{226}Ra, weak and negative relationship between ^{40}K and ^{232}Th while fair and negative relationship between ^{226}Ra and ^{232}Th.Mean values for absorbed dose rate in air D ($nGy\ h^{-1}$) and outdoor annual effective dose E ($mSv\ y^{-1}$) were found lower than the UNSCEAR safety limit of 60 $nGy\ h^{-1}$ and 0.07 $mSv\ y^{-1}$ respectively.

Calculated external hazard index and internal hazard index and alpha index for urea fertilizer in this study were found higher than urea fertilizers (D.3, D.4, D.5) used in Iraq (Nada *et al.,* 2020). Alpha index for the study ranged from 0.046 to 0.117 with mean value of 0.077 which varied from the result reported from agriculture fertilizers in Iraqi markets by Akram (2021). However, external hazard index, internal hazard index and alpha index for urea fertilizer in this study were found lower than the safety standard of unity (1.0) as observed from Table 1. The radiological parameters calculated suggested that the use of urea fertilizer investigated for multipurpose do not pose significant radiological risk to the users. Therefore, the urea fertilizer samples investigated are radiologically safe, so fear of radiological impact to buyers' sellers, factory workers, gardeners, truck drivers and loaders of the urea fertilizer samples should not be entertained.

This study did not determine the radium equivalent activity concentrations (Ra_{eq}) for urea fertilizer, due to the fact that urea fertilizer should not be used for building or construction of houses for residence or buildings for other purposes. Studying larger sample size would have been good enough to generalize in the country, Nigeria.However, they may not be significant variation from this study in the study area as the measuring instruments and statistic used are valid and reliable.

CONCLUSION

Human beings are continuously, unconsciously and consciously exposed to ionizing radiation emanating from radioactive elements found in materials which may be or may not be harmful to human cells. Radiological hazard indices associated with the use of urea fertilizer by factory workers, buyers, sellers of the product, farmers and gardeners was investigated using NaI(Tl) gamma ray spectrometer detector. Results showed that urea fertilizer samples investigated were safe for use. Therefore, fear of radiological sickness through exposure pathways to human being and its immediate environment or surrounding should not be entertained for now. Manufacturers, buyers, sellers and farmers should limit the length of time spent in the radiation field (Factories; markets, farms and lawns). Further investigation in other parts of the country, Nigeria is recommended so as to compare and contrast.

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