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Research Article

Activity Concentration of Natural Radioactivity and Dose Assessment for Brands of Chemical Fertilizers used in Iraq

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Abstract

The aim of the present work is to measure the activity concentration of naturally occurring radionuclides ^{40}K, ^{226}Ra and ^{232}Th in different brands of fertilizer samples in Iraq using Germanium detector gamma spectrometry. The results of measurements showed that the mean of specific activities for ^{226}Ra, ^{232}Th and ^{40}K activities in the all fertilizers are 181.5, 119.92 and 2508.34 Bq/kg, respectively. With respect to NPK (Nitrogen, Phosphor and Potassium) fertilizers under investigation, the average radioactivity of ^{226}Ra, ^{232}Th and ^{40}K are 341.73, 248.63 and 5166.43 Bq/kg, respectively. Some of radium equivalent activity is exceeding 370 Bq/kg, the maximum permissible limit for radiation dose, others are not exceeding for present samples. Average values of the natural radionuclides measured in the brands of chemical fertilizers used in Iraq are higher the range of values reported in several other countries. This study could be useful as baseline data for radiation exposure to fertilizers and their impact on human health.

Keywords: *^{238}U, ^{232}Th and ^{40}K radionuclides, chemical fertilizer, environmental radioactivity*

Introduction

In order to access high agricultural productivity, the current practice of replacing nutrients in soils and consequently supplying substances is done by the application of chemical fertilizers, mostly compounds commercially named NPK (nitrogen (N), phosphorus (P) and potassium (K)) and NPKs (sulfate based fertilizer), the phosphorus portion in these fertilizers taken from phosphate rocks, which are containing various amounts of natural radioactive elements (Ashraf *et al*, 2001; Skorovarov *et al*, 2000). During phosphate ore manufacturing, due to chemical properties of Radium, practically all ^{226}Ra gets included into phosphogypsum and remains in disequilibrium status when compared to radioactivity levels contained in the raw material. Most of the phosphogypsum is considered waste and is stored or discharged into the aquatic environment (UNSCEAR, 2000). Potential issues of concern resulting from phosphogypsum disposal are its environmental impacts; possible increases in radionuclides in soils or in groundwater and consequential ingestion by humans through exposure routes such as drinking water and food chain (Laich, 1991).

Many types of fertilizers are used in Iraq like: Super Phosphate, Urea Sulfate, and Ammonium Nitrate Sulfate. Utilization phosphate fertilizers over a period of many years could eventually increase the radium and uranium content of the soil and consequently increase the radiation dose which would result in the corresponding increase of the dose and causes cancers for human body (Righi *et al*, 2005). Also, during handling, packing and transporting fertilizers, some workers can receive additional external exposure at dose rates up to 0.8 $mGy \cdot h^{-1}$(Abbady *et al*, 2005).

Once deposited in bone tissue, ^{226}Ra has a high potential for causing biological damage through continuous irradiation of human skeleton over many years and may be cause bone sarcoma (Marovic and Sencar, 1995).

The interest natural radionuclides are mainly potassium, uranium, thorium, and the radionuclides that are created as their radioactive decay chains. Emanation of radon gas (e.g., ^{222}Rn and ^{220}Rn of lifetimes 3.8 d and 55.6 s, respectively) into air occurs as a product of uranium ^{238}U and thorium ^{232}Th decay chains, respectively. The short lived decay products of radon are responsible for most of the hazards by inhalation. The hazard of radon comes from its radioactive progeny, which use their physical properties to spread or attach like dust do, trapped in the lung and depositing their alpha-particle energies in the tissue, producing higher ionization density than beta particles or gamma-rays. Lung cancer, skin cancer, and kidney diseases are the health effects attributed to inhalation of radon-decay products (Kumar *et al*, 1986).

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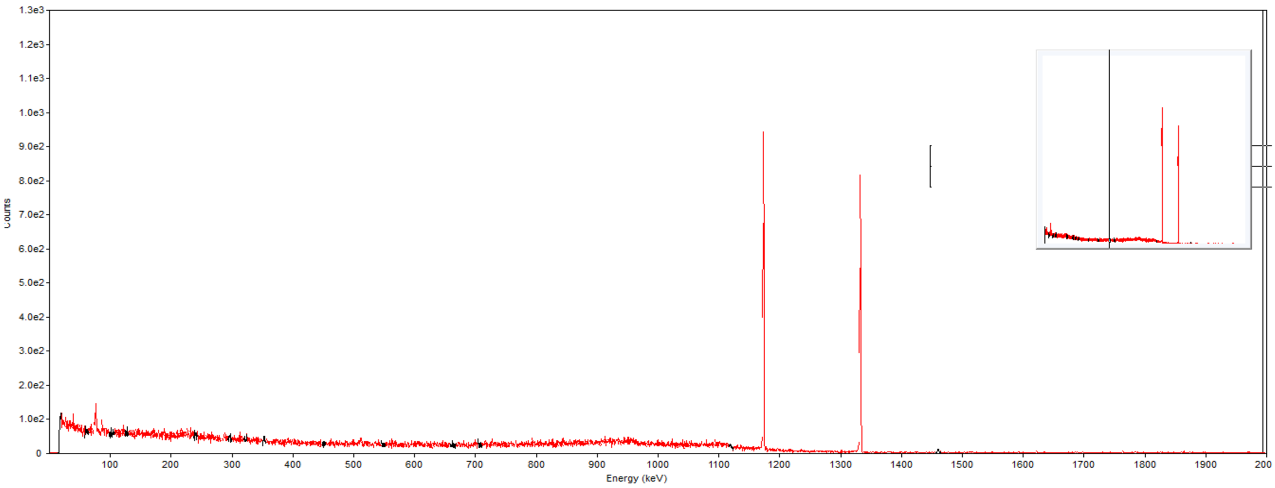

Fig. 1: Calibration spectrum for Ge(Li) detector using Co-60

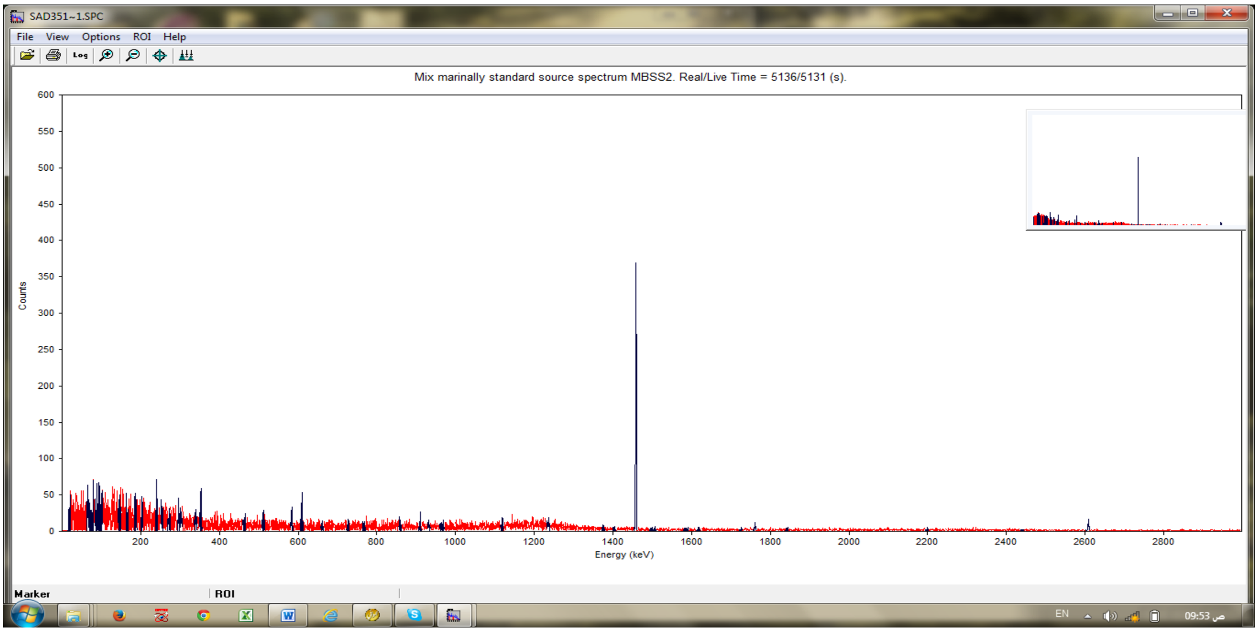

Fig.2: Spectrum of chemical fertilizer sample type 8.

The radiological impact from the above nuclides is due to radiation exposure of the body by the gamma rays and irradiation of the lung tissues from inhalation of radon and its progeny (Papastefanou *et al*, 1983).

From the natural risk point of view, it is important to measure natural radioactivity in fertilizers and by-products, because the high radioactive content may lead to significant exposure of miners, manufacturers and end users. Furthermore, such measurements provide basic data for the estimation of the amount of radioactivity spread on agricultural land along with fertilizers.

The aim of this work are: 1) determine the activity concentrations of naturally occurring radionuclides in a famous chemical fertilizer samples, which are available samples in Iraqi markets, 2) provide a useful information in the monitoring of environmental contamination by natural radioactivity.

Experimental Work

Nine samples of different brands were collected from the local market of Baghdad City; all samples are chemical fertilizers. The code type and other information about these samples are summarized in Table1. The chemical fertilizer which are used by majority farmers Iraqis $CO(NH_2)_2$, Compound Mg, Nitro, Compound ($NZNNH_4P_2O_5Fe$), and Compound ($NP_2O_5K_2O$) with Other compounds. All the brands of fertilizer are solid. After collection, the samples were ground, pulverized to fine powdered material, heated in the oven at 80˚C for 24 h to remove moisture and then sealed in plastic containers. The samples were left a side for a month to allow the attainment of uranium and thorium radioactive equilibrium. The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for all equilibrium samples were measured by a gamma ray spectrometry using well advanced piece of equipment produced by ORTEC hand held Ge(Li) detector with an overall efficiency better than 42%. The resolution of this detector is 1.32185 MeV for Co-60 energy. The energy calibration of Ge(Li) gamma-ray spectrometer is performed by Co-60 radioactive source as shown in Fig.1. Detector employed with adequate lead shielding which reduces the background radiation. In addition all samples spectra are corrected by subtracting the background radiation by using Eq. 1.

$$\text{Background (Bq)} = \frac{Area}{IY\%\ EFF\ \%\ Tc} \quad (1)$$

where, Area: The neat area under the peak, count
I_Y% : The branching ratio for photon energy
Eff: Efficiency of the Ge(Li) detector.
Tc : The total counting time interval in seconds
But the specific activity for samples has been measured using:

$$\text{Specific Activity (Bq)} = \frac{(Area-Bg)/Tc}{IY\%\ Eff\ \%\ m}$$

where m: The mass of samples

Theoretical Calculations

1. Calculation the Activity Concentrations

The gamma ray lines for natural radionuclides were determined using gamma spectrum for chemical fertilizer as shown in Fig.2. The specific activity of ^{238}U it is found from gamma-ray lines of ^{226}Ra, ^{214}Bi at 609.3keV and ^{214}Pb at 295.2 and 351.92 keV, while the specific activity of ^{232}Th was evaluated from gamma-ray lines of ^{212}Pb at 238.6 keV, ^{228}Ac at 911.1 keV. The specific activity of ^{40}K was determined directly from its 1460.8 keV gamma-ray line (Joga *et al*, 2008).

2. Radium Equivalent Activity (Bq/kg)

In order to assess the activity level of ^{226}Ra, ^{232}Th and ^{40}K in fertilizer, a common radiological index has been defined in terms of radium equivalent activity (Ra_{eq}) in Bq·kg^{-1} can be used , provides a very useful guideline in the organization safety standards in radiation protection for a human population. The index was calculated through Eq.2 is based on the assumption that 370 Bq·kg^{-1} of ^{226}Ra, 259 Bq·kg^{-1} of ^{232}Th and 481 Bq·kg^{-1} of ^{40}K produce the same gamma-ray dose rate (Beretka and Mathew, 1985):

$$Ra_{eq}\left(\frac{Bq}{kg}\right) = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (2)$$

3. Absorbed and Effective Dose

The measured activity of ^{226}Ra, ^{232}Th and ^{40}K were converted into doses (nGy·h^{-1} Bq^{-1}·kg^{-1}) by applying the factors 0.462, 0.604 and 0.0417 for radium, thorium and potassium, respectively. These factors were used to calculate the total absorbed gamma dose rate in air at 1 m above the ground level using the Eq.3 (UNSCEAR, 2000).

$$Absorbed\ dose\ D\left(\frac{nGy}{h}\right) = 0.462C_{Ra} + 0.604C_{Th} + 0.041C_K \quad (3)$$

where C_{Ra}, C_{Th} and C_K are the activities (Bq·kg^{-1}) of radium, thorium and potassium in the samples. To estimate annual effective doses, must be taken into account of 1) the conversion coefficient from absorbed dose in air to effective dose and 2) the indoor occupancy factor. The annual effective doses are determined using Eq. 4 (UNSCEAR, 2000):

$$\text{Outdoor annual effective dose (mSv)} = D\left(\frac{nGy}{h}\right) \times 8760h \times 0.2 \times \frac{0.7Sv}{Gy} \times 10^{-6} \quad (4)$$

Annual estimated average effective dose equivalent received by a member is calculated using a conversion factor of 0.7 Sv·Gy^{-1}, which is used to convert the absorbed rate to annual effective dose with an outdoor occupancy of 20% (UNSCEAR, 1993).

Results and Discussion

Table1 represents the concentrations of natural radionuclides in chemical fertilizers which are studied in the present work and their types and properties.

Table1: Types and properties of chemical fertilizers and the concentrations of Natural radionuclides

Code Type	Fertilizers properties	Radionuclides	Energy (keV)	Activity (Bq/kg)
1	Composite B-N Iraqi DAP	Ra-226	186.10	511.45
		Pb-212	238.6	266.56
		Pb-214	295.21	259.93
		Pb-214	351.92	259.92
		Bi-214	609.31	226.96
		Bi-214	1120.29	198.37
		Bi-214	1280.96	386.45
		K-40	1460.75	2003.53
2	Composite B-N Jordan DAP	U-235	143.76	28.71
		U-235	185.71	37.05
		Pb-214	351.92	12.83
		Bi-214	609.31	13.81
		Bi-214	934.06	22.70
		K-40	1460.75	24.77
3	Iraqi Urea	Zr-95	16.62	61.32
4	NP Nitrogen group Zn+Fe+P_2O_5+NH_4+N Antalya	U-235	202.11	112.68
		Pb-212	238.6	181.86
		Bi-214	1120.29	52.46
		Bi-214	1407.98	47.39
		K-40	1460.75	6710.93
		Bi-214	1764.49	30.45
		Bi-214	1847.42	17.55
		Bi-214	2204.21	33.42
5	Composite Nitro Jordan	Pb-214	351.92	0.79
		Ac-228	909.67	186.40
		Bi-214	1120.29	46.15
		K-40	1460.75	2245.7
		Bi-214	1764.49	22.05

		Bi-214	2204.21	4.3
6	NPK Chlorine free [N+P_2O_5+K_2O] Imported	Ra-226	83.78	215.54
		Pb-212	238.6	310.91
		Ac-228	911.1	182.69
		Bi-214	1120.29	8.9
		K-40	1460.75	6027.82
		Bi-214	1729.59	34.65
		Bi-214	1764.49	36.91
7	NPK Imported	Pb-212	74.81	5.94
		Pb-212	87.30	108.71
		Ac-228	129.07	141.17
		Pb-212	238.63	314.65
		Ac-228	270.24	81.39
		Pb-212	300.09	394.02
		Ac-228	338.32	73.33
		Ra-226	449.37	0.0036
		Pb-214	487.08	467.92
		Pb-214	839.03	994.95
		Ac-228	968.97	6.74
		K-40	1461.00	4305.04
8	Composite Mg Spanish	Pb-214	351.92	1.10
		K-40	1460.75	40.62
9	Iraqi DAP B+N	Pb-212	77.11	12.71
		Ac-228	129.07	37.67
		Pb-214	295.21	12.61
		Pb-214	351.92	4.28
		Ac-228	409.46	50.24
		Pb-214	462.10	281.60
		Ac-228	794.95	10.99
		Ac-228	911.21	18.94
		K-40	1461.00	1216.70

The measured concentrations of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K in fertilizer samples are shown in Table 2. In chemical fertilizers, the concentration of ^{226}Ra varies from ND (not detection) to 511.4 Bq·kg^{-1} with an average value of 181.5Bq·kg^{-1}, the concentration of ^{232}Th varies from ND to 314.56Bq·kg^{-1} with an average value of 119.92 Bq·kg^{-1}, whereas the concentration of ^{40}K exists in the range from ND – 6710.93 Bq·kg^{-1} with an average value of 2508.34 Bq·kg^{-1}. For the NPK fertilizer, the average activity of ^{226}Ra, ^{232}Th and ^{40}K are 341.73, 248.63 and 5166.43 Bq/kg, respectively. The results showed that the NPK fertilizers have the highest emitter of the radiation in comparison with the other samples under study.

Table 2: The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (Bq/kg) in chemical fertilizers

Code Type	Concentration of Ra-226 (Bq/kg)	Concentration of Th-232 (Bq/kg)	Concentration of K-40 (Bq/kg)
1	511.4	266.56	2003.53
2	13.81	ND	24.77
3	ND	ND	ND
4	52.46	181.86	6710.93
5	72.50	186.40	2245.7
6	215.54	182.69	6027.82
7	467.92	314.56	4305.04
8	1.10	ND	40.6
9	299.05	117.24	1216.70
Average	181.5	119.92	2508.34

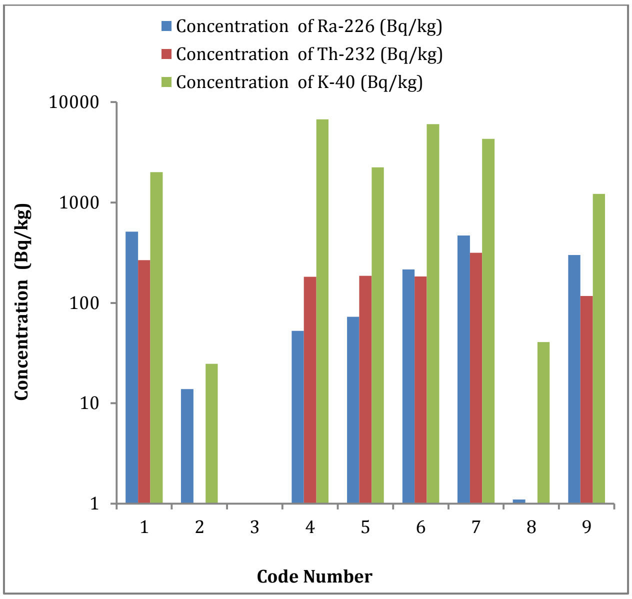

Fig.3: The activity concentration of Ra-226, Th-232 and K-40 in chemical fertilizers

Table 3, presents, the range value of radium equivalent activity (Ra_{eq}) for chemical fertilizers varied from ND to 1249.22 Bq·kg^{-1} with an average value 573.18 Bq·kg^{-1}, and for NPK the average value 1095.07 Bq·kg^{-1}, therefor, the radium equivalent activity is exceed 370 Bq/kg, the maximum permissible limit for radiation dose. The NPK fertilizers which contain high natural radiation are imported and not an Iraqi-made.

Table 3: Radium equivalent, absorbed dose and dose equivalent for different samples

Code Type	Ra_{eq} (Bq/kg)	Absorbed dose (D) (nGy/h)	Outdoor annual effective dose (mSv)
1	1046.85	479.41	0.5897
2	15.72	7.41	0.0091
3	ND	ND	ND
4	829.26	411.91	0.505
5	511.97	239.05	0.293
6	940.93	459.48	0.564
7	1249.22	584.40	0.72
8	4.23	2.18	2.698×10^{-3}
9	560.39	259.34	0.3181
Average	573.18	271.46	0.334

The absorbed and annual effective dose rates from the samples were calculated as shown in Table 3 and Figs.4 and 5. The minimum and maximum values of absorbed dose and outdoor annual effective dose in the chemical samples studied in the present work were found to vary from ND to 584 nGy·h^{-1} with an average value 271.46 nGy/h, and ND to 0.72 mSvy^{-1} with an average value 0.334 mSvy^{-1}, respectively. The larger value given for the absorbed dose rate is of 55 nGy/h (24 - 85 nGy/h (UNSCEAR, 1988). A more recent UNSCEAR report gave wide range (18 - 93 nGy/h) with an average value of 59 nGy/h (UNSCEAR, 2000). The results showed that absorbed dose rate for the chemical fertilizer samples are higher than the world limits, but the effective dose rates for all samples were not exceed the recommended value 1 mSv. Therefore, all the samples analyzed in the present work satisfy the safety criterion for general public (ICRP, 1991). Hence, most of these samples do not pose much health hazard for the population.

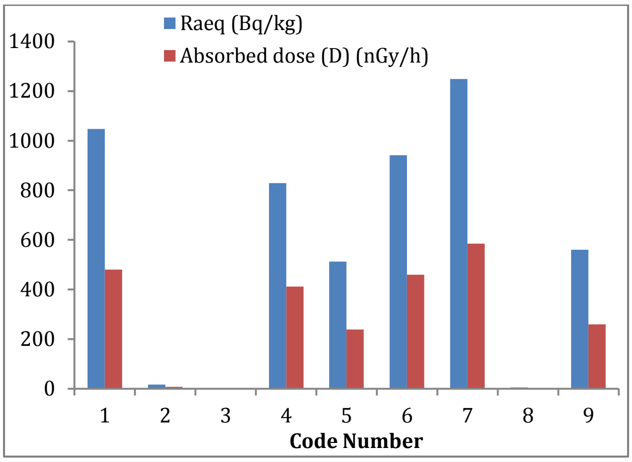

Fig.4: The Radium equivalent and absorbed and annual effective dose rates from the chemical fertilizer

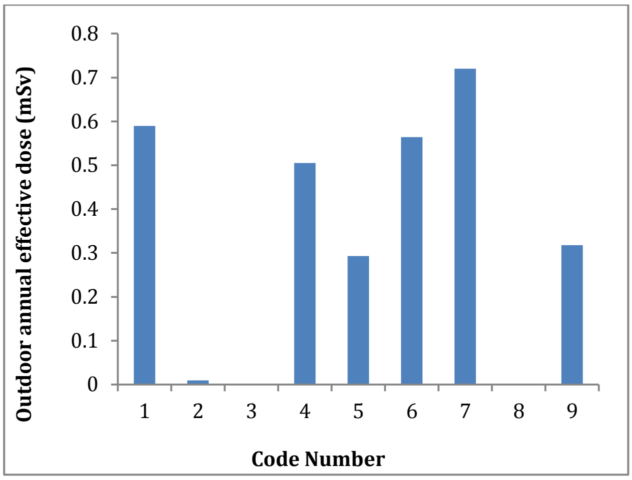

Fig.5: The outdoor annual effective dose (mSv) from the chemical fertilizer

Figures 3 and 4, describe the average activity of ^{226}Ra, ^{232}Th, ^{40}K (Bq·kg^{-1}) and the radium equivalent with absorbed dose of different fertilizer used in Iraq, respectively. Table 4 shows average concentrations of the radionuclides in our study compared with the reported values from other countries.

Table 4: Comparison of activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in Iraqi NPK fertilizer samples and other countries

Country	Ra-226	Th-232	K-40	Ra_{eq} (Bq/kg)	Reference
Egypt	366	67	4	462	(Ahmed and El-Arabi, 2005)
India	79	28	1042	198	(Chauhn, *et al*, 2013)
Germany	520	15	720	597	(Khan *et al*, 1996)
Nigeria	143	9	2729	366	(Jibiri1 and Fasae, 2012)
Brazil	420	80	153	546	(Saueia, 2005)
Finland	54	11	3200	316	(Mustonen, 1985)
Saudi Arabia	64	17	2453	275	(Alharbi, 2013)
USA	780	49	200	865	(Gulmond and Windham, 1975)
Iraq	341.73	248.63	5166.43	1095.86	Present work

It is found that for NPK fertilizers the average ^{226}Ra concentration of (341.73 Bqkg^{-1}) is lower than activity concentration values of Egypt, Germany, Brazil and USA samples, and higher than India, Nigeria, Finland and Saudi Arabia samples.

The average ^{232}Th concentration of (248.63 Bq·kg^{-1}) is found higher than all the reported concentration from Egypt. The average ^{40}K concentration of (1095.86Bq·kg^{-1}) is higher than all the values reported concentrations.

Conclusions

Concentrations of ^{226}Ra, ^{232}Th and ^{40}K in nine fertilizer samples collected from Baghdad city (Iraq) have been measured using gamma spectrometry. Average concentrations of ^{226}Ra, ^{232}Th and ^{40}K are 64, 17 and 2453 Bq·kg^{-1}, respectively. These values have been compared with the world wide reported data. The result showed that the highest values presented in chemical fertilizers and the lowest values were found in the organic fertilizers. Some radium equivalent activity for present samples was below and others are above the recommended limits (370 Bq·kg^{-1}). From the calculated value it is recommended to use Iraqi fertilizer rather than imported fertilizers.

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