



Original Article

Radiometric examination of fertilizers and assessment of their health hazards, commonly used in Pakistan

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ARTICLE INFO

Article history:

Received 29 October 2022

Received in revised form

23 February 2023

Accepted 17 March 2023

Available online 30 May 2023

Keywords:

Fertilizers

Radionuclides

Gamma spectroscopy

Radiological health hazards

Excessive lifetime cancer risk (ELCR)

ABSTRACT

The radioactivity concentrations of Naturally Occurring Radioactive Materials (NORM) i.e., ²²⁶Ra, ²³²Th, and ⁴K in various chemical fertilizers being used in the agricultural soil of Pakistan were determined utilizing gamma spectrometry by employing a High Purity Germanium (HPGe) detector. The radioactivity concentrations of ²²⁶Ra, ²³²Th, and ⁴K extended from 2.58 ± 0.8 – 265.7 ± 8.8 Bq kg⁻¹, 1.53 ± 0.14 – 76.6 ± 1.07 Bq kg⁻¹ and 36.5 ± 1.34 – 15606.7 ± 30.2 Bq kg⁻¹ respectively. The radiological hazard parameters such as internal and external indices and annual effective dose rates were calculated, while excessive lifetime cancer risk factors for the indoor and outdoor areas were found in the range from 0.3×10^{-3} to 10.723×10^{-3} and 0.03×10^{-3} to 2.7948×10^{-3} of most fertilizers, however, some values were slightly higher than the UNSCEAR (The United Nations Scientific Committee on the Effects of Atomic Radiation) recommended values for potash-containing fertilizers such as MOP (Muriate of Potash).

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1. Introduction

NORMs (Naturally Occurring Radioactive Materials) are commonly found in our environment, such that rocks, soil, water, fertilizers, and vegetation. The common sources of these NORMs are uranium, thorium, and potassium. Usually, uranium and thorium also contain radium and radon as their decay products. A constant impact of these ionizing radiations may cause light to severe or lethal damage to human health depending upon the severity of the radiations. NORMs may cause redness of the skin, DNA (Deoxyribo Nucleic Acid) damage, mutation of cells, and finally leads to cell killing. A new terminology, TENORM (Technology Enhanced Naturally Occurring Radionuclide Material) includes coal mining, oil and gas extraction, fertilizers industry and building industry pose a significant increase in the concentrations of NORMs

in the atmosphere and nature. Many experiments on plants and animals have deduced that ionizing radiation may also cause genetic mutation in humans and can cause illness and death within weeks of exposure [1]. Radiation is also valued in research, health, and industries in this modern era. High exposure to radiation carries a risk, but we can't avoid it entirely as radiation has always been a part of our environment. Before the mid-21st century, the global population is expected to reach nine billion. In current times to ensure global food security, fertilizers are being used majorly worldwide to meet food production [2]. Approximately half of the world's crop production is based on fertilizers. Almost 48% of the population consumes food produced by applying nitrogen fertilizers to increase food production [3]. Fertilizers are used to attain the desired nutrient level in the soil for the crops throughout the seasons. If nutrient deficiency occurs, the production of the crop gets affected. Ninety-Two (92) natural nutrients are present in plants, but out of them, 17 are considered essential [4]. Pakistan produces fertilizers domestically and imports them too. Ammonium Sulphate (AS), Calcium Ammonium Nitrate (CAN), and Urea are made locally in Pakistan as straight nitrogen fertilizers. Single

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Super Phosphate (SSP) is the only straight Phosphate Fertilizer, and Nitro Phosphate (NP) is a complex fertilizer [5]. All types of samples from local markets are collected and used in Pakistan. The increased use of fertilizers may disturb the surface water, soil, and groundwater because of the dispersal of minerals. The radioactive elements of fertilizers vary significantly and hinge on their concentrations in the parent mineral and on the process of fertilizer manufacturing together. ²³⁸U concentrations can vary between 7 and 100 pCi/g in phosphate rock and 1–67 pCi/g in phosphate fertilizers [6]. Where elevated yearly phosphorus fertilizer rates are cast off, it can ensure ²³⁸U concentrations in sewerage waters and soils much larger than usually existing. The radioactivity concentration of usually used radionuclides provides valuable information to examine environmental pollution. In this paper, the presence of radioactivity in fertilizers and their health hazards have been targeted to know whether they are being used within safe limits given by UNSCEAR-2000 [7]. The Excessive Lifetime Cancer Risk (ELCR) is an additional possibility that a person may develop cancer if that person is exposed to additional cancer-causing materials for a longer time. The ELCR was calculated to estimate the probability of cancer incidence in a population of individuals [8].

2. Materials and method

Fifteen samples of indigenous fertilizers mainly used in Pakistan were collected from the local market and placed in airtight sealed plastic bags to measure the presence of radioactivity in them. The collected samples were crushed into fine powder to remove the larger grain sizes and make the selection homogenous. The powdered samples were dried up in an oven at 110 °C for eradication of any moisture if present. Then 1 kg of each fertilizer sample was put in Marinelli beakers. The Marinelli beakers were then tightly sealed with wrapping tapes to avoid every possibility of releasing radon. The sealed containers of all samples were placed for forty days to gain the secular equilibrium between radionuclides ²²⁶Ra, ²³²Th and their daughter isotopes [9].

²²⁶Ra, ²³²Th, and ⁴K radionuclide radioactivity concentrations in samples were measured via the High Purity Germanium Detector (HPGe). The system contains a detector (NGC-5022) HPGe detector attached to a Multi-Channel Analyzer (MCA) with a built-in spectroscopy amplifier installed in a PC and the GAMMA-W software. The HPGe detector is in a cylinder-shaped lead (Pb) shielding, 10 cm thick, having an inside lining of copper (Cu), Aluminum (Al), and Perspex. HPGe detectors have the advantage over other types of gamma detectors. It has good resolution power as compared to NaI(Tl) scintillator detector. Because of its high resolving power, it can resolve low energy spectrum. The detector's efficiency was

Table 1
Gamma-ray energies and percentage abundances corresponding to the respective spectral peaks.

Parent Nuclide	Daughter Nuclide	Gamma Ray Energy (keV)	Abundance (%)
²²⁶ Ra	²¹⁴ Pb	351.92	35.1
	²¹⁴ Pb	295.21	19.2
	²¹⁴ Pb	241.98	7.12
	²¹⁴ Bi	609.32	44.6
	²¹⁴ Bi	1764.52	15.1
	²¹⁴ Bi	1120.28	14.7
	²¹⁴ Bi	1238.11	5.78
	²¹⁴ Bi	768.3	4.46
	²³² Th	²¹² Pb	238.63
²²⁸ Ac		911.16	26.6
²²⁸ Ac		968.97	16.23
²²⁸ Ac		338.42	11.26
²⁰⁸ Tl		583.19	84.5
²⁰⁸ Tl		2614.5	54.06
⁴ K	⁴ K	1460.8	10.67

roughly 52.3% and shows a good resolution of 1.85 keV [10]. The system was calibrated for energy with point sources using the RG1 reference materials of ¹³⁷Cs (661.615 keV), ²⁴¹Am (59.536 keV), and ⁶⁰Co (1173.231 keV). The background readings for spectra were collected for 15,000 s every 2–3 weeks to certify the detector's performance. Spectrum procurement for every sample of fertilizers was taken for 15,000 s and was saved in a computer. After performing spectrum analysis with GAMMA-W software, radioactivity concentrations of samples were computed by subtracting the background from the sample's spectrum counts against each gamma peak. The study of the radionuclides was based on the peaks of the gamma-emitting by daughter products in equilibrium with their parent nuclei [11,12].

3. Radiometric examination

3.1. Radioactivity concentration

A precise measurement has been done to measure the activity concentration of ²²⁶Ra, ²³²Th, and ⁴K using the formula in equation (1) [13,14].

$$\text{Radioactivity Concentration} = \frac{\text{Net Count}}{(\epsilon \times I_{\gamma} \times T \times M)} \text{ Bq kg}^{-1} \tag{Eq 1}$$

Where ϵ represents the absolute gamma peak efficiency of the detector at the specific gamma-ray energy, I_{γ} is the decay intensity of the specific energy peak, T is the count time for the measurement in seconds, and M represents the mass of the sample in kg. The radioactivity concentrations of ²²⁶Ra, ²³²Th, and ⁴K were assessed from the peaks of their progenies, having several gamma rays with different Photo peak efficiencies and energies. The peaks of their progenies' energy and abundance are given in Table 1 [15].

The radioactivity concentration of ²²⁶Ra, ²³²Th, and ⁴K of all the samples were calculated using equation (1) and tabulated in Table 2. However, setting a limit of detection for each energy is essential when dealing with low-level radiation measurements. The Currie derivation is often used to calculate the minimum detectable activity per sample unit of mass for a specific radionuclide with a 95% confidence level, and it is in accordance with ISO 11929 and ISO 10703 requirements [16]. In our study, the Minimum Detectable Activity (MDA) of the HPGe detector is approximately 1.5 Bq/Kg.

3.2. Radium equivalent radioactivity

The calculation of radioactivity concentration of ²²⁶Ra ²³²Th, and ⁴K does not specify any hazard, so to observe the effect of exposure radium equivalent radioactivity (R_{eq}) was determined by using the following formula [17].

$$R_{eq} = (A_{Ra}) + (A_{Th} \times 1.43) + (A_K \times 0.077) \text{ Bq kg}^{-1} \tag{Eq 2}$$

A_{Ra} , A_{Th} , and A_K are the radioactivity concentrations of ²²⁶Ra, ²³²Th, and ⁴K correspondingly in Bq kg^{-1} . When talking about radium equivalent radioactivity, it is presumed that the 370 Bq kg^{-1} of ²²⁶Ra, 259 Bq kg^{-1} of ²³²Th, and 4810 Bq kg^{-1} of ⁴K yield similar dose rates [18].

3.3. Absorbed dose rate and annual effective dose

The absorbed gamma dose in the air at 1 m over the ground surface for the even dispersal of radionuclides naturally prevailing was calculated by using the formula underneath [19,20].

Table 2
Measured radioactivity concentration of ²²⁶Ra, ²³²Th, and ⁴K samples of fertilizers gathered from the market in Pakistan.

S. No	Sample	²²⁶ Ra Bq kg ⁻¹	²³² Th Bq kg ⁻¹	⁴⁰ K Bq kg ⁻¹
1.	Boron	2.58 ± 0.8	4.41 ± 0.2	100.50 ± 1.21
2.	DAP	–	–	–
3.	Urea	10.50 ± 0.17	3.85 ± 0.5	133.7 ± 1.72
4.	Ammonium Nitrate	–	–	2817.4 ± 12.3
5.	MAP	6.10 ± 0.38	–	72.72 ± 1.7
6.	SOP	–	–	13706.6 ± 31.2
7.	MOP	–	–	15606.7 ± 30.2
8.	NPK (Z)	–	–	3112.7 ± 12.4
9.	NPK	–	–	3694.2 ± 15.4
10.	Ammonium Sulphate	60.5 ± 7.5	–	–
11.	SSP	129.01 ± 1.9	–	–
12.	Zn Sulphate	2.7 ± 0.08	1.53 ± 0.14	36.5 ± 1.34
13.	Nitro Sulphate	265.7 ± 8.8	76.6 ± 1.07	–
14.	Zinc Nitrate	4.8 ± 0.07	1.68 ± 0.1	142.6 ± 2.1
15.	CAN	4.3 ± 0.71	6.4 ± 0.78	121.3 ± 1.9
	Average	54.02 ± 2.26	15.74 ± 0.46	3594.99 ± 10.13

$$D_{out} = (A_{Ra} \times 0.462) + (A_{Th} \times 0.604) + (A_K \times 0.417)nGyh^{-1} \tag{Eq 3}$$

$$D_{in} = (A_{Ra} \times 0.92) + (A_{Th} \times 1.1) + (A_K \times 0.08)nGyh^{-1} \tag{Eq 4}$$

Where, 0.462, 0.604, 0.417, 0.92, 1.1 and 0.08 are the use conversion factor with SI unit *nGyh⁻¹*. A_{Ra}, A_{Th}, and A_K are the radioactivity concentrations of ²²⁶Ra, ²³²Th, and ⁴K in Bq kg⁻¹, respectively.

The Annual Effective Dose (AED) was evaluated using the absorbed gamma dose rates and the dose conversion factor of 0.7 SvGy⁻¹ by an outdoor and indoor occupancy factor of 0.2 and 0.8 correspondingly and calculated with the following equations [21].

$$E_{out} = D_{out} \times 1.227 \times 10^{-3}mSvy^{-1} \tag{Eq 5}$$

$$E_{in} = D_{in} \times 4.908 \times 10^{-3}mSvy^{-1} \tag{Eq 6}$$

3.4. Internal and external health hazards

After determining the annual effective dose for the common public, we calculate the internal and external health hazards. The relation below is used to assess the internal hazard index [21,22].

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{Eq 7}$$

The external hazard index was calculated by the relation given below:

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{Eq 8}$$

A_{Th}, A_{Ra}, and A_K are the radioactivities of ²³²Th, ²²⁶Ra, and ⁴K correspondingly, in Bq kg⁻¹. The external hazard index necessarily is less than 1 to retain γ -radiation dose less than 1 mSv y⁻¹.

3.5. Representative level index

This indicator (RLI) Representative Level Index is linked to the specific radioactive elements in the building commodities and has been used to assess the amount of Gamma-radiation risk [21].

$$I_{yr} = [(A_{Ra} / 150) + (A_{Th} / 100) + (A_K / 1500)] \tag{Eq 9}$$

3.6. Excessive lifetime cancer risk

The ELCR was calculated to estimate the probability of cancer incidence in a population of individuals. There is always a chance of 33% (or 0.33% per person) that an individual will be diagnosed with cancer at some stage of life due to normal exposure to natural radioactivity and or a toxic substance [1] The Department of Environmental Quality (DEQ) considers a chance of 1 in 100,000 persons. That means 1 × 10⁻⁵ is the allowable limit [22]. ELCR is an additional possibility that a person may develop cancer if that person is exposed to additional cancer-causing materials for a longer time. The indoor ELCR(in) was calculated to estimate the total ELCR. Both ELCR(in) and ELCRout) are vital parameters for calculating of cancer incidence in a population. Excess lifetime cancer risk assesses the additional risk of cancer tempted by exposure of an individual to ionizing radiations [23,24].

Mathematically,

$$ELCR_{out} = E_{out} \times DL \times RF \tag{Eq 10}$$

$$ELCR_{in} = E_{in} \times DL \times RF \tag{Eq 11}$$

Where E is the annual effective dose, DL is the average duration of a person's life (70 years), and RF is the risk factor specified as 0.051 by ICRP [22–28].

4. Results and discussion

Table 2 displays the measured radioactivity concentration of ²³²Th, ²²⁶Ra, and ⁴K in fertilizer samples collected from the market. Subsequently, the gamma-specific radioactivity of all models was measured with an HPGe detector. From Table 2, it can be perceived that radioactivity concentration of ²³²Th, ²²⁶Ra, and ⁴K ranges from (2.586–129.05) Bq kg⁻¹, (1.538–76.62) Bq kg⁻¹, and (36.52–3694.23) Bq kg⁻¹ correspondingly. The results show that ²²⁶Ra radioactivity of the fertilizers such as Ammonium Sulphate, SSP, and Nitro Sulphate have slightly higher concentrations because chemical fertilizers are reinforced with ²²⁶Ra and ²³²Th along with the decay products. Potassium Sulphate and Nitro Phosphate Potash are enriched in ⁴K, and there is no potassium content in Ammonium Phosphate and Di Ammonium Phosphate.

For a fair comparison of the radioactivity concentration in these fertilizers, Radium equivalence is used. The values are given in Table 3. These values vary from 6.06 Bq kg⁻¹ for SSP to 1200 Bq kg⁻¹ for NPK (Z). The safe limit for Ra_{eq} for NORM is stated by Occupational Committee on Radiation Development OECD-1979 and

Table 3
Internal and external radiological health hazards of the samples of fertilizers collected from the market of Pakistan.

Fertilizer Name	Req (Bq kg ⁻¹)	H _{in}	H _{ex}	D _{in} (nGyh ⁻¹)	D _{out} (nGyh ⁻¹)	E _{out} (mSvy ⁻¹)	E _{in} (mSvy ⁻¹)	I _{yr}
Boron	16.62	0.05	0.04	7.64	8.05	0.01	0.04	0.13
DAP (Di-ammonium Phosphate)	16.63	–	–	–	–	–	–	–
Urea	–	0.1	0.07	12.3	12.76	0.02	0.06	0.20
Ammonium Nitrate	26.3	0.59	0.59	112.7	117.49	0.14	0.55	1.88
MAP (Mono-ammonium phosphate)	216.73	0.05	0.03	5.72	5.85	0.01	0.03	0.09
SOP (Sulphate of Potash)	11.7	2.85	2.85	548.27	571.57	0.7	2.69	9.14
MOP (Muriate of Potash)	1054.36	3.24	3.24	624.27	650.8	0.8	3.06	10.40
NPK (Z)	1200.52	0.65	0.65	124.51	129.8	0.16	0.61	2.08
NPK (Nitro Phosphate Potash)	239.45	0.77	0.77	147.77	154.05	0.19	0.73	2.46
Ammonium Sulphate	284.17	0.03	0.02	2.79	2.8	–	0.01	0.40
SSP (Single Super Phosphate)	6.06	0.7	0.35	59.35	59.61	0.07	0.29	0.86
Zn Sulphate	129.02	0.04	0.03	4.96	5.11	0.01	0.02	0.06
Nitro Sulphate	10.76	1.73	1.01	164.4	169.07	0.21	0.81	2.54
Zn Nitrate	375.25	0.06	0.05	8.88	9.23	0.01	0.04	0.14
CAN (Calcium Ammonium Nitrate)	18.27	0.07	0.06	10.36	10.92	0.01	0.05	0.17
Average	257.56 ± 16.1	10.86 ± 3.3	9.76 ± 3.12	130.30 ± 11.41	136.22 ± 11.67	0.18 ± 0.05	0.64 ± 0.07	2.18 ± 0.9

should not be more than 369.9 Bq kg⁻¹ [11]. The values of Ra_{eq} for all samples were seen within limits except for NPK (Z) and MOP (Muriate of Potash), which were above safe limits, as shown in Fig. 1.

The values for dose rate vary from 2.79 nGyh⁻¹ to 624.27 nGyh⁻¹ indoors and 5.11 nGyh⁻¹ to 650.80 nGyh⁻¹ outdoors, as shown in Fig. 2. Most of the values were above the worldwide average values, which are 59 nGyh⁻¹. The H_{in} and H_{out} for all the samples vary from (0.02–3.24 mSvy⁻¹) and (0.05–3.24 mSvy⁻¹), as shown in Fig. 3.

The data indicate that SOP (Sulphate of Potash), MOP (Muriate of Potash), and Nitro Sulphate have higher values than safety limits. The value for External Hazard Index has to be less than 1 mSvy⁻¹ [29,30]. The AED (Annual Effective Dose) rate value (E_{in} and E_{out}) varies from (0.04–2.69 mSvy⁻¹) and (0.01–0.80 mSvy⁻¹) in Table 3, which is higher than the safety limits proposed by UNSCEAR [31] as shown in Fig. 4. The measured values for the Excess Lifetime Cancer Risk for indoors and outdoors range from (0.3 × 10⁻³ to 10.723 × 10⁻³) and (0.03 × 10⁻³ to 2.7948 × 10⁻³), respectively in Fig. 5. Fig. 6 illustrates the Representative Level Index for our

studied fertilizer samples with SOP (Sulphate of Potash) and MOP (Muriate of Potash) having higher values because of higher ⁴K radioactivity concentration.

Fig. 7 shows a typical gamma spectrum of a DAP sample. The dominant peaks are marked by their energy peaks. The data obtained from HPGe Gamma-W software and further analyzed using Fitz Peak Software and the final spectrum obtained as shown in Fig. 7.

Table 3 shows the radium equivalent, annual effective dose rate, indoor and out hazards, Representative Level Index, and the excessive lifetime cancer risk.

5. Comparison with similar studies

The radioactivity concentrations as well as the Radium equivalent radioactivity and representative level index in samples from the examined region and fertilizers were compared with comparable research in other countries, and the summary of results is shown in Table 4.

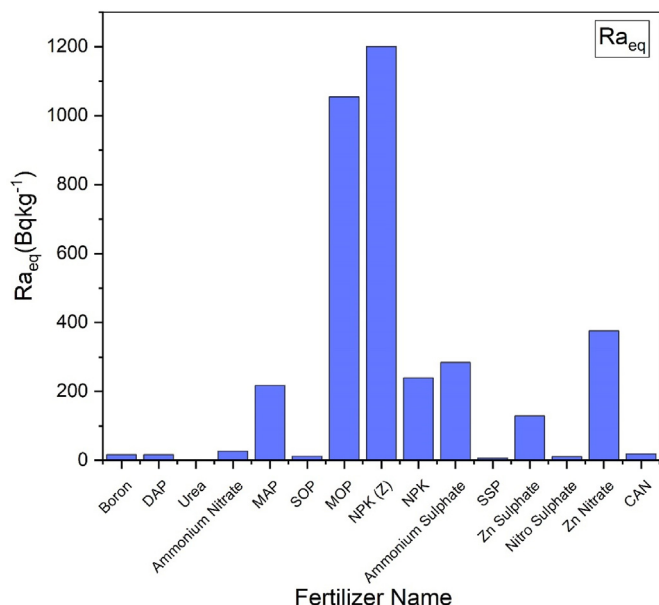


Fig. 1. Illustrating the Radium equivalent in Bq kg⁻¹ of various samples of fertilizers.

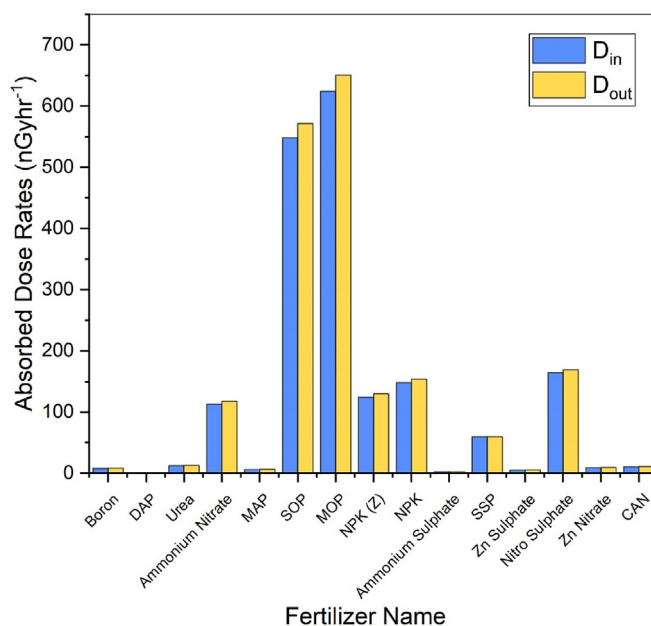


Fig. 2. A comparison of absorbed dose rate D_(in) and D_(out) in nGyh⁻¹ of the fertilizers used in Pakistan.

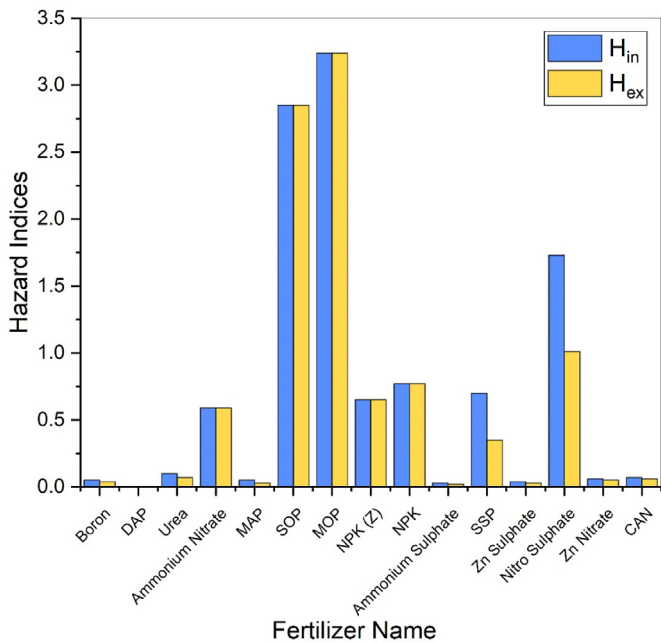


Fig. 3. A comparison of internal hazard and out door $H_{(in)}$ and $H_{(out)}$ in of the fertilizer's samples.

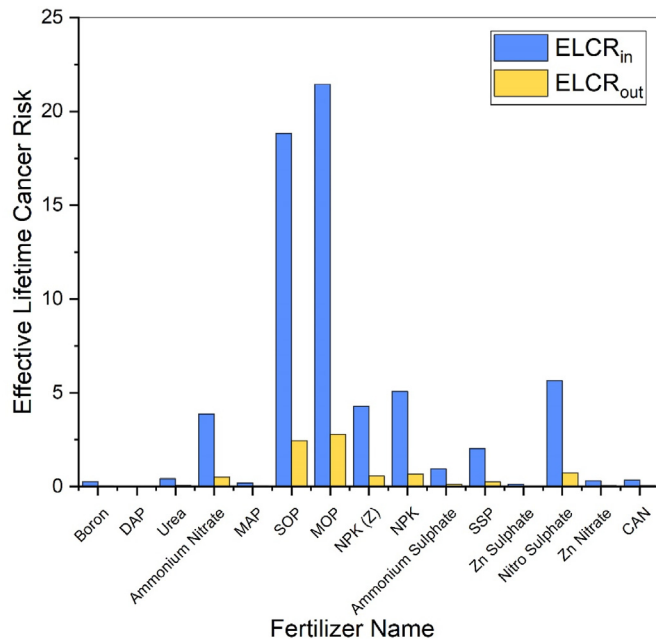


Fig. 5. A comparison of Excessive life Lifetime Cancer Risk ELCR (in) and ELCR (out) in fertilizers samples.

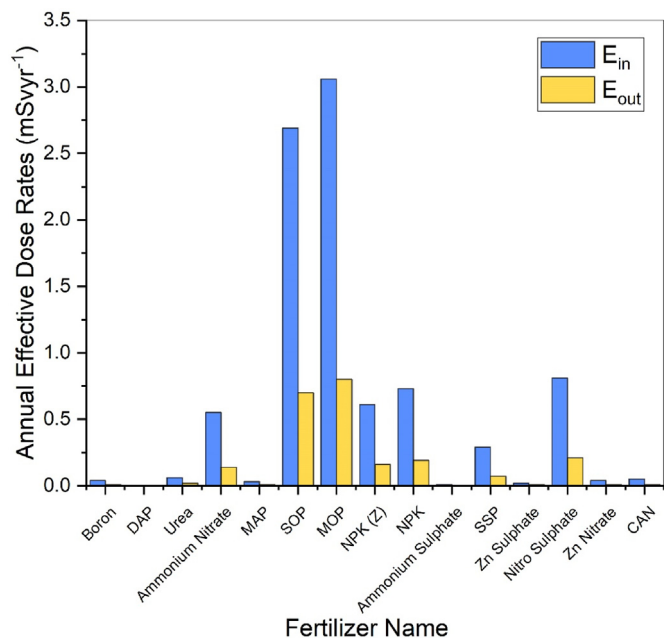


Fig. 4. A comparison of Annual Effective Dose $E_{(in)}$ and $E_{(out)}$ of fertilizers in $mSvyr^{-1}$.

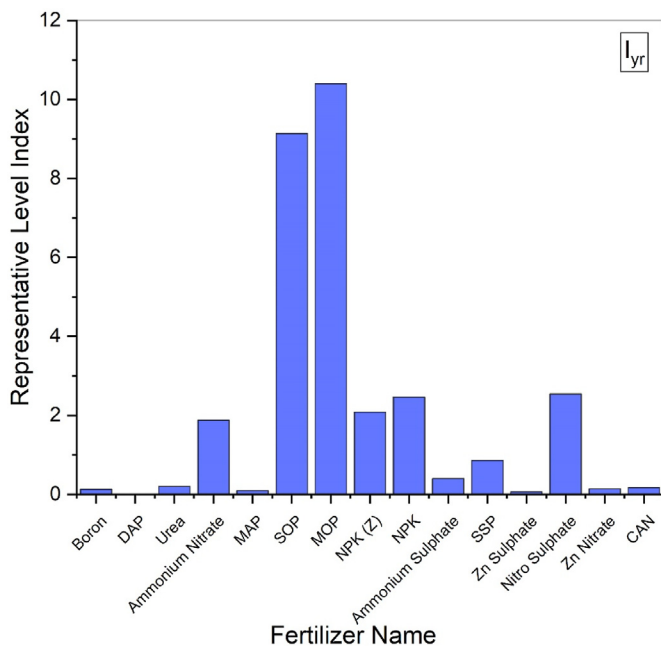


Fig. 6. Illustrating the representative level index of various samples of fertilizers.

The UNSCEAR study from 2000 states that the radioactivity concentration for 4K in the globe for fertilizers is 23–12324 $Bq\ kg^{-1}$ with an average of 4860 $Bq\ kg^{-1}$ [30–34]. For the area under inquiry, the measured value of radioactivity concentration of 4K falls under the global average. In comparison to non-fertilized soil, fertilized soil has higher values.

6. Conclusion

The natural radioactivity of the fertilizers samples in Pakistan is determined by using the HPGe gamma-ray spectrometer. The

outcomes show that there is no drastic change in the values of most of the fertilizers that can cause severe damage. However, the values are a little bit higher for some of the fertilizers having potash in them, which can increase the health risks, e.g., an increase in cancer probability. The result of the study indicates that the usage of the chemical fertilizers in farmlands to upsurge the production of crops rises the radioactivity concentration of natural radioactive nuclides, particularly Potassium Sulphate, Nitro Phosphate Potash (NPK), and NPK(Z), Ammonium Super Sulphate with a high concentration of ^{226}Ra , ^{232}Th and 4K . The value for indoor absorbed dose varies from 4.96 $nGyh^{-1}$ to 624.27 $nGyh^{-1}$ and 5.11 $nGyh^{-1}$ to 650.80 $nGyh^{-1}$

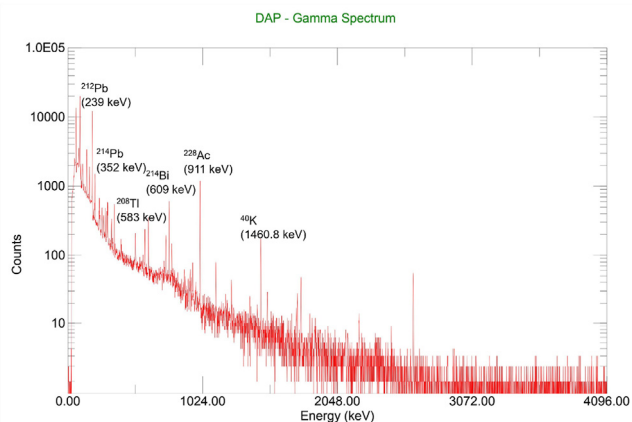


Fig. 7. Gamma Spectrum of sample obtained by HPGe showing gamma peaks of a fertilizer sample.

Table 4 Comparison with similar studies.

Country	Sample	Activity (Bq/kg)			Radium equivalent (Bq/kg)	Level index I _{yr}	Reference
		Ra ²²⁶	Th ²³²	K ⁴⁰			
Pakistan	Chemical Fertilizers	32.4	6.3	2636.29	240.39	2.04	Present Study
Algeria	NPK fertilizer	134.7	131.8	11644	1168	9.6	[30]
Egypt (Qena)	Phosphate fertilizer	366	66.7	4	461.7	3.1	[31]
Brazil (Panama)	Virgin soil	1.69	5.36	34.15	12	0.1	[32,33]
Brazil (Panama)	Fertilized soil	10.22	7.27	54.75	24.8	0.2	[32,33]
Brazil (Panama)	NPK fertilizer	647.6	753.9	603	1772.1	12.3	[32,33]
Pakistan (Pakka Anna)	Virgin soil	26	50	500	—	—	[20]
		-31	-55	-610			
Pakistan (Pakka Anna)	Fertilized soil	30	50	560	—	—	[20]
		-38	-64	-635			

for outdoor absorbed dose. The values of H_{in} and H_{ex} for all the samples vary from (0.02–3.24) and (0.05–3.24). The Annual Effective Dose rate value (E_{in} and E_{out}) varies from (0.04–2.69 mSv⁻¹) and (0.01–0.80 mSv⁻¹). The values for the Excess Lifetime Cancer Risk (ELCR) for outdoor and indoor range from (0.3 × 10⁻³ to 10.723 × 10⁻³) and (0.03 × 10⁻³ to 2.7948 × 10⁻³), respectively. The calculated values of radium equivalent were 6.02 Bq kg⁻¹ to 1200.52 Bq kg⁻¹. The values of Radium Equivalent were higher for MOP ((Muriate of Potash) and NPK (Z). Moreover, the values of absorbed dose and Annual Effective Dose (AED) were higher than the limits for SOP, MOP, and Nitro Sulphate. The Excess Lifetime Cancer Risk (ELCR) values were higher than the recommended limits of UNSCEAR for SOP and MOP fertilizers. The values are higher than the recommended limits due to the high content of potassium in these fertilizers. The current study reveals that these kinds of fertilizers should be restricted or limited utilization as use of fertilizers in the soil to minimize the dangerous effects on human beings.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors acknowledge the support provided by King Abdullah City for Atomic and Renewable Energy (KA CARE) under K.A. CARE King Abdulaziz University Collaboration Program. This research work was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant number (IFPIP:18-135-1443). Therefore, the authors gratefully acknowledge technical and financial support provided by the ministry of education and king Abdulaziz university, DSR, Jeddah, Saudi Arabia.

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