Dose Estimate of radon radioactive pollutants in samples of phosphate fertilizers and pesticides

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Abstract. Proceeding from the fact that agriculture is a long process of intensification through which society sought to meet its ever-increasing needs for food, and the necessity of countries to meet the needs of their populations, which made them resort to various means to meet these needs and as a result of the steady increase in the use of phosphate fertilizers in particular so that agriculture does not become a cause of exacerbation of environmental pollution with materials Radioactive substances and toxins that pose a significant danger to human life and living organisms, with the accompanying dangerous pathological phenomena. This research measured the concentration of radioactive pollutants in phosphate fertilizers. A s well as analyzing the radon levels in phosphate fertilizers and pesticide samples obtained from marketplaces in Iraq. Radiological parameters were measured using nuclear track detectors to calculate yearly effective exposure levels and the corresponding cancer risk. The acquired data were compared to the UNSCEAR's recommended limits and were determined to be within them.

1 Introduction

Crops generally depend on the soil to supply water and dissolved nutrients needed for plant growth through the soil solution that the plant absorbs through its root system spread in the soil. For plant growth, directly or indirectly, it is called fertilizers to increase soil fertility. For farmers to realize the importance of fertilization, and from the year 1960 A.D., and with the progress in fertilization technology and the use of mineral nutrition, crops began to improve in quantity and quality in most regions of the world, especially the developed ones, because fertilization improved properties Natural and chemical agricultural lands, in addition to intensive farming systems, improving the characteristics of agricultural products, increasing vertical expansion in crop production, and increasing production. The following categories can be used to categorise fertilisers: organic fertilisers, all fertilisers produced naturally and used in their original state. They include animal fertilizers containing a high percentage of organic matter and some necessary nutrients [1-3]. They also contain living organisms that decompose organic matter. These fertilizers are characterized by improving the acidity of the soil. They are cultivated and ploughed in the soil to improve their properties,

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the most important of which are nitrogen-fixing leguminous crops and organic fertilizers, which include farm, slaughterhouse, and sewage waste [4]. Chemical fertilizers are fertilizers made by man with special techniques and contain nutrients in an inorganic form. They can be divided into simple fertilizers containing one nutrient element, which is the element to which fertilizer is added. The most common of them is nitrogenous fertilizer, which is the fertilizer that supplies plants and soil with the nitrogen element that is considered the first of the most important main fertilizer elements needed by the plant in the form of ammonium NH_4 or the form of nitrate NO_3 or the form of amides or a combination of forms together such as ammonium sulfate and urea, and its nitrate form and urea are easy to lose more than the ammonium form when increasing irrigation rates and therefore it is possible to determine the validity of any including according to the degree and liquidity of solubility in water [5]. And phosphate fertilizers, which are fertilizers that contain phosphorus as an essential element in it and must be added to the land, especially in the lands of dry and desert areas due to intensive farming systems and continuous irrigation, which causes symptoms of phosphorus deficiency, which is the second most important basic element necessary for soil fertility and plant growth, it is slow moving and is not easily washed from the ground like water Nitrogenous fertilizers [6, 7]. Also, phosphorus compounds lead to the precipitation of some rare elements present in the agricultural soil that the plant needs and convert them into compounds that are insoluble in water in addition to minerals. However, their effect may extend for millions of years. Therefore, the focus will be on them exclusively in this study. Potash fertilizers contain potassium As a fertilizer element, the third most important element of soil fertility and compensates for what was lost from it. However, the land must be fertilized with ammonium nitrogen fertilizer and not waste irrigation water to raise the efficiency of using potassium fertilizers in desert lands such as potassium chloride and potassium nitrate. Potassium is the third most important element for soil fertility and compensates for what was lost from it [8]. As for complex fertilizers, they contain more than one fertilizer element, especially those that contain the three major elements, such as NPK fertilizer, and may contain some other necessary elements. Fertilizers can also be divided according to the nature of Fertilizers are divided into solid fertilizers, such as those previously mentioned, and other liquid fertilizers that are used in the form of solutions dissolved in water and sprayed on plant leaves, and gaseous fertilizers, the most important of which is CO_2 fertilizer, which has recently been used in greenhouses and growth rooms to increase the rate of photosynthesis and improve productivity [9].The list of elements necessary for plant growth has increased over the past years, and the total of these substances is now about 16. The plant takes the first three elements (H, O, C) from water and air and therefore is not included in manufacturing fertilizers. In comparison, the remaining six major elements are divided into major elements. Primary (N, P, K) and major secondary elements (Ca, S, Mn) [10]. In addition to the sixteen previous elements, some other elements, such as silicon Si, sodium Na, and cobalt Co, are necessary to increase crop yield or improve crop value for human and animal nutrition. Among the terms you need to know To study chemical fertilizers, it is the grade or grade, which means the fertilizer content of nutrients, which is expressed in weight percentages of N, P_2O_5, and K_2O. At the same time, in most countries, it indicates only the number of materials found by approved analytical methods [11]. It is written on the fertilizer envelope and its arrangement is fixed and unchanged, so the first ratio will be for nitrogen N, the second for phosphorous P or phosphorous Pentax ide P_2O_5, the third for potassium, the fourth for calcium Ca, the fifth for magnesium Mn, and the sixth, if any, will be for the microelements and write + microelements, so if we find on the fertilizer envelope, for example, it is written 15 -15-30, it indicates that the fertilizer contains from its weight 15% P_2O_5, 15% N, 30% K_2O, and in the absence of any element, a zero is written in its place, while the fertilizer ratio indicates the ratio of the elements composing the fertilizer to each other, and therefore the fertilizer ratio will be for (15-15-30) is (1-1-2) [12] , while

Fertilizer Nutrient denotes one of the three major plant nutrients K, N, P, and denotes any food in the United States and Plant Nutrient It represents a group of manufactured elements as elements necessary for plant growth, whether they are major, secondary or minor elements, the lack of which negatively affects the plant in terms of its growth and production [13]. Phosphate ore, used as a raw material in producing fertilizers, typically contains varying levels of naturally occurring radioactive elements [14]. Phosphate is a form of phosphorous mineral and expresses a salt of phosphoric acid. It represents one of the mineral resources of some countries of the world. Its presence is important for vital systems as a structural material for bones and teeth. [15], where phosphate is interacted with acids to produce Super phosphate and nitrogen phosphate, in addition to the possibility of extracting some rare metals and radioactive elements. Uranium-238, for example, is a side product that can be obtained when converting phosphate into fertilizers or phosphoric acid. Studies have shown that Arab phosphate deposits contain huge amounts of uranium that can be extracted from phosphoric acid as a product Secondary [15]. Phosphate rock has the decay sequences of U and Th. Based on each element's solubility and chemical properties, radionuclides migrated to intermediate, final, and by-products during the industrial process. As a result, it is critical to assess natural radioactivity in phosphate rock and various fertilizers and products because high radioactive concentrations may expose miners, manufacturers, and end users to severe risk [16]. Desert phosphate ores contain 200g of uranium-238 per ton, which makes it an important resource that is increasingly in demand by the majority due to its entry into several manufacturing industries, the most important of which are chemical fertilizers, especially in nations interested in agricultural production and food security, which is to some extent linked to their ability to obtain These fertilizers as a factor to raise the amount of agricultural production quantity and quality even [17]. many researchers study the radionuclides in phosphate fertilizers [18-21] . This study uses a CR-39 detector to measure the radon concentration (the daughter of 238U) in several samples of phosphate fertilizers purchased from the Iraqi market.

2 Materials and Methods

This research used a solid-state nuclear track detector to study the radon concentration in samples of phosphate fertilizers. Using the sealed cup technique and a CR-39 detector, phosphate fertilizer samples were positioned at the base of a cylindrical seal that was 7 cm high and 5 cm in diameter, had a thickness of 1 mm, density of 0.32 gm/m3, and dimensions of 2.5cm x2.5cm. CR39 is an appropriate material since it is an accurate, transparent solid-state nuclear track detector (SSNTD)[22]. Additionally, CR-39 is immune to X-rays and electromagnetic pulses found in our environment, ensuring a strong alpha particle signal in the experiment. Track Analysis Systems Ltd. provided the transparent, colourless, and stiff CR-39 used in this project. The plastic container, which was tightly covered and exposed to radon for 30 days, had the detectors mounted to the top. Detectors were removed from the containers after exposure and put in a NaOH solution at 6.25 N in a water bath at 75 degrees F within four hours. [23, 24] [.The track density was calculated using the method within the TASLIMAGE program, which TASL designed in the nuclear physics lab at Kufa University's Department of Physics.

3 Measurements of hazard indices

3.1 Radon concentration

The following equation calculates the radon concentration (C) in surrounding samples in Bq/m3. [8, 25].

$$C(Bq.m^{-3}) = \frac{C_o(Bq.day.m^{-3})}{\rho_o(Track.cm^{-2})}\left\{\frac{\rho(Track.cm^{-2})}{t(day)}\right\} \quad \ldots\ldots\ldots\ldots..(1)$$

And standard deviation σ_n (S.D.):

$$\sigma_n(S.D.) = \sqrt{\frac{\sum_i^n (X_i - \overline{X})^2}{n-1}}$$

C = the concentration of ^{222}Rn in the test container air above the sample in (Bq/m3).while C_o represents the exposure of the samples in Bq.day.m^{-3}. ρ_0: Track density (number of tracks.cm-2) of detectors calibrated to the samples under investigation .ρ:From track density concentration of radon (C_{Rn}) was calculated using the sensitivity factor[8, 26]:

$$C_{Rn}\ (Bqm^{-3}) = \frac{\rho}{kxt} \ldots\ldots\ldots(2)$$

k: calibration factor equals 0.19 (tr.cm^{-2})/ d. (Bq.m^{-3}); t: exposure time (30 d).

3.2. The Potential Alpha Energy Concentration (PAEC)[25]:

$$PAEC\ (WL) = F \times C_{Rn}\ /\ 3700 \quad \ldots\ldots (3)$$

F = 0.4 in this research

3.3. Exposure to Radon-222 progeny (E.P.) [27]:

$$E_P\ (WLM\ Y^{-1}) = 8760 \times n \times F \times C_{Rn}\ /\ 3700 \times 170 \ldots\ldots(4)$$

Where C_{Rn} (Bq.m^{-3}), n = (0.8), 8760 is the number of hours per year, and 170 is the number of hours per working month. The excess lifetime cancer risk (ELCR) due to radon exposure [28]

$$ELCR = E_P \times DL \times F \quad \ldots\ldots\ldots\ldots.(5)$$

DL: life expectancy (70 y); F: risk factor equal to 0.0551.Sv^{-1}

3.4 The annual effective dose (AED) :

$$AED\ (m\ Sv/y) = C_{Rn} \times F \times n \times 8760 \times D \ldots\ldots\ldots (6)$$

n=0.8, D = 9×10^{-6} (m Sv)/(Bq. m^{-3}. h)

3.5. The lung cancer cases per year per million person (CPPP)

$$(CPPP) = AED \times (18 \times 10^{-6}\, mSv^{-1}.y) \ldots\ldots\ldots (7)$$

4 Result and Discussion

Fertilization constitutes one of the essential variables determining crop growth and production, and governments depend on it to meet their population's expanding food needs. Therefore, it is necessary to pay attention to agriculture so that agriculture does not become a source of threat to humans and living organisms because it is an additional reason for increasing environmental pollution. It is also known that phosphate reservoirs contain Radioactive pollutants and harmful or highly toxic metals if they are present in specific concentrations and are usually associated with phosphate rock. Moreover, Iraq has reservoirs of phosphate rock, and it must import fertilizers from industrialized countries. Therefore, it was necessary to conduct studies to ensure that the fertilizers available in the markets are free of pollutants and measure The number of contaminants, if any, and tighten control over all food imported from abroad. The sample information and the radon concentrations measured in the phosphate fertilizers and pesticide samples are included in Table 1.

Table 1: The types and codes of fertilizer and pesticide samples studied.

Code of samples	Fertilizer and pesticide type	Code of samples	Fertilizer and pesticide type
C1	shoot	C11	NPK Granules
C2	Man colax	C12	Sulphur –dusting fungicide
C3	Master power	C13	Master flour
C4	Carbaryl Chemical Compound	C14	Vector(chania)
C5	Norwegian Chemical / Root Fertilizer	C15	Di ammonium phosphate
C6	NPK 10-20-10 . Granular Compound Fertilizer	C16	ORTs 509 mg
C7	NPK Powder	C17	ATLAS
C8	agricultural sulfur	C18	Qanas super
C9	NPK 10 20 10+6S (Chemical Magnesium)	C19	EDTA iron sodium salt(Hunan, China)
C10	DAP(NH4)2(HPO4)	C20	Master Power Phosphoric Acid

The results for the radon concentration values of the examined phosphate fertilizer and pesticide samples are shown in Table 2. The minimum value of ^{222}Rn in the phosphate fertilizer samples was equal to 35.09 Bq/m^3 in sample coded C8in agricultural sulfur, and the highest value of ^{222}Rn was equal to 818.71 Bq/ m^3 in sample coded C15 in Di ammonium phosphate. The current results show that ^{222}Rn in fertilizer samples is greater than the globally permitted level according to UNSCEAR 2000 **[27]**(see Figure 1).

Table 2: Alpha track density. Radon concentration and number of radon atoms in fertilizer samples

Code Samples	*Alpha track density*	*Radon concentrations Bq/m^3*	*Radon atomsx10^{-10}*
C1	106.67	187.13	5.83561E-05
C2	200.00	350.88	3.11232E-05
C3	133.33	233.92	4.66849E-05
C4	66.67	116.96	9.33697E-05
C5	53.33	93.57	0.000116712
C6	46.67	81.87	0.000133385
C7	333.33	584.80	1.86739E-05
C8	20.00	35.09	0.000311232
C9	166.67	292.40	3.73479E-05
C10	40.00	70.18	0.000155616
C11	300.00	526.32	2.07488E-05
C12	60.00	105.26	0.000103744
C13	73.33	128.65	8.48816E-05
C14	86.67	152.05	7.18229E-05
C15	466.67	818.71	1.33385E-05
C16	100.00	175.44	6.22465E-05
C17	146.67	257.31	4.24408E-05
C18	53.33	93.57	0.000116712
C19	66.67	116.96	9.33697E-05
C20	400.00	701.75	1.55616E-05
Mix	-	282.93	-
Min	-	35.09	-
World	-	534.892	-

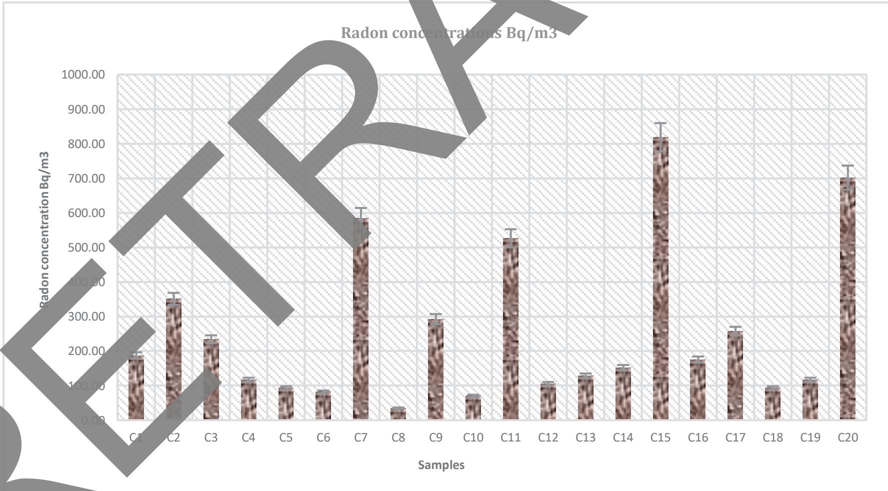

Fig. 1. Comparison between values of radon concentration Bq/m3 in all Fertilizer and pesticide samples in research understudies

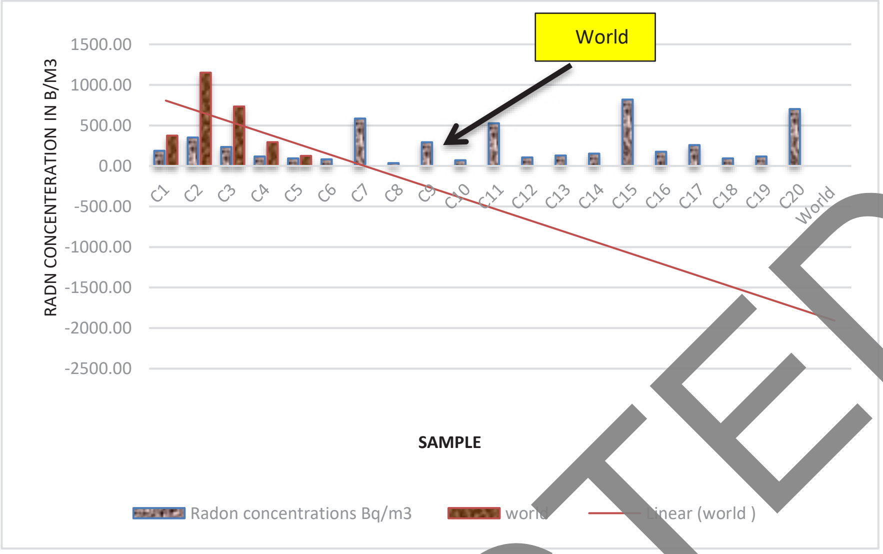

Fig. 2 . Comparison between values radon Bq/m3 in all Fertilizer and pesticide samples and world value in references [27]

Figure 2 compares the results gained in this study to those presented in a reference [27], where the results showed higher percentages of radon in samples similar to those studied in this study, which could be due to a difference in measurement technique. Table 3. calculated the annual effective dose (AED)from equation(6)in mSv per year with a maximum value of 2.06 mSv per year in sample C15 (Di ammonium phosphate DAP) contains both Nitrogen and Phosphorus, while the minimum value of 0.088 mSv per year in sample C8 (agricultural sulfur). Table 3 shows the Potential Alpha Energy Concentration (PAEC), the high value in sample C15 but the low value found in sample C8. These values were compared with the global values contained in the report of the UNSCEAR and other international research, and they were very few.

Table 3: Annual effective dose (AED) and excess lifetime cancer risk (ELCR), E.P. (WLM Y-1), PAEC, and CPPP.

Code of sample	*AED* (mSv/y)	E_P($WLM\ Y^{-1}$)	PAEC	ELCR*10^{-3}	(CPPP)*10^{-6}
C1	0.472117895	10.28	0.02	1.817653895	184.9591282
C2	0.885221053	19.27	0.04	3.408101053	346.7983653
C3	0.590147368	12.84	0.03	2.272067368	231.1989102
C4	0.295073684	6.42	0.01	1.136033684	115.5994551
C5	0.236058947	5.14	0.01	0.908826947	92.47956409
C6	0.206551579	4.50	0.01	0.795223579	80.91961858
C7	1.475368421	32.11	0.06	5.680168421	577.9972755
C8	0.088522105	1.93	0.01	0.340810105	34.67983653
C9	0.737684211	16.06	0.03	2.840084211	288.9986378
C10	0.177044211	3.85	0.01	0.681620211	69.35967307
C11	1.327831579	28.90	0.06	5.112151579	520.197548
C12	0.265566316	5.78	0.01	1.022430316	104.0395096
C13	0.324581053	7.06	0.01	1.249637053	127.1594006
C14	0.383595789	8.35	0.02	1.476843789	150.2792916

C15	2.065515789	44.96	0.09	7.952235789	809.1961858
C16	0.442610526	9.63	0.02	1.704050526	173.3991827
C17	0.649162105	14.13	0.03	2.499274105	254.3188012
C18	0.236058947	5.14	0.01	0.908826947	92.47956409
C19	0.295073684	6.42	0.01	1.136033684	115.5994551
C20	1.770442105	38.53	0.08	6.816202105	693.5967307
Max	2.065515789	44.96	0.08	7.952235789	809.1961858
Min	0.088522105	1.93	0.003	0.340810105	52.67983653

The minimum value of E.P. in unit WLM Y-1 was 1.93 in sample C8(agricultural sulfur), while the maximum value was 44.96 in sample C15(Di ammonium phosphate). Table (3) also shows that radon-induced (CPPP) was found to range from 52.67983653x10-6 per year per million person to 809.1961858x10-6 per year per million person. It is a higher value than the value declared by the World Health Organization. Table(3) also shows that ELCR associated with radon exposure of the population was determined using the equation based on the methodology described in equation 6; the results ranged from 7.952235789 x10-3 in sample C15 (Di ammonium phosphate) to 0.340810105 x10-3 in sample C8(agricultural sulfur). It is a higher value than the value declared by the UNSCEAR. Correlation values between AED and CPPP were calculated, and the correlation was very strong (0.99)

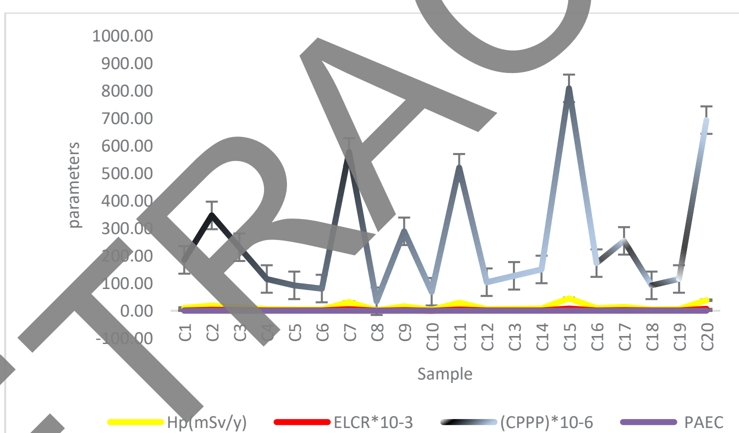

Fig. 3: Correlation between all Samples with all parameters E.P., ELCR, CPPP, and PAEC.

From the figure3 above, we notice that the values of CPPP were very high compared with the rest of the variables under study, which are values that depend mainly on the absorbed doses of radon, and this indicates the high effect of radon concentration in fertilizers and pesticides. Figure (4) shows the Histogram, the Q-Q plot, and the boxplot to distribute the concentration of radon in Fertilizer and pesticide samples, we can see that the distribution of radon concentration was a non-normal distribution in which the Kolmogorov–Smirnov test failed to assess the normality, and this is clear from the Q-Q plot of radon distribution in which the observed values deviate from the standard line. The boxplot of radon concentration indicates two outliers (C20 and C15), and the top whisker is longer than the bottom, meaning that the distribution of radon concentration has highly positive skewness.

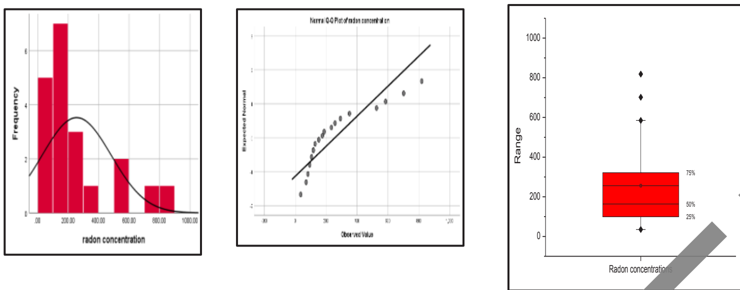

Fig. 4: The histogram and Q-Q plot of the radon concentration for studied samples

5 Conclusion

This search measured the radon concentration and some radiological parameters for Phosphate Fertilizer and pesticide samples. The radon concentration was less than the recommended and allowed limit by the UNSCEAR except for samples coded C7, C15, and C20. AED and EP results for all samples were lower than the global allowable limit. CPPP and ELCR results that due to radon exposure had values highest the global allowable limit in sample C15.

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