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Distribution of primordial radionuclides in phosphate fertilizers and rock deposits of Pakistan

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ABSTRACT: *Gamma emitting radionuclides due to ^{40}K, ^{226}Ra and ^{232}Th in different domestic as well as imported phosphate containing fertilizers, used in Pakistan, have been determined. For measurement, analysis and data acquisition a high purity germanium detector and PC based MCA was used. The measured values of the specific activity due to ^{226}Ra were found to be very high and varied from 307.7 to 617.5 $Bq.kg^{-1}$. The minimum and maximum values of the radium equivalent activities for different brands of phosphatic fertilizers resulting from all the three detected gamma emitting radionuclides were estimated to be 338.8 $Bq.kg^{-1}$ and 929.8 $Bq.kg^{-1}$ respectively. This enhanced level of radioactivity can cause a significant radiation exposure if these fertilizers are handled in places with poor ventilation system and consequently can lead to radon accumulation. Moreover, this data can also be utilized to assess hazards of radioactivity being spread along with phosphate containing fertilizers in soil during various agricultural processes.*

INTRODUCTION

Our planet, Earth, is permanently exposed to ionizing radiation of both terrestrial and extra-terrestrial origin. Radioactivity is present everywhere in nature and almost any sample of rock, water and air will show its presence if placed in a sufficiently sensitive device for detection. Thus man is exposed to these radionuclides in varying degrees, depending upon his activities and location.

Natural and man-made sources of radiation result in internal and external doses to the public. According to UNSCEAR (UNSCEAR, 1988) in normal back ground areas about 54% of the total external dose received by the public originates from ^{40}K, ^{226}Ra (a member of ^{238}U decay series) and ^{228}Ra (a member of ^{232}Th decay series), which makes them important for dose assessment. From bioenvironmental point of view, the most significant radionuclide is ^{40}K (half life = $1.28x10^{9}$ years and isotopic abundance = 0.0118%). A 70 kg man contains about 140 g of potassium, mostly in the muscles, which corresponds to 4.4 kBq of ^{40}K in the body (Kathren, 1998). Different isotopes of Thorium include Th from mass no. 227 to mass no. 232 in which naturally occurring thorium, as found in nature, is essentially 100%, ^{232}Th by weight (half life = $1.39x10^{10}$ years). The adult human body contains about 0.80 Bq of ^{232}Th. The important isotopes of Radium are Ra^{226} (half-life=1602 years) 94.6%, ^{223}Ra (half-life=11.4 days) 9%, ^{224}Ra (half-life=3.64 days) 94% and ^{228}Ra (half-life=6.7 years) 100% branching ratio. Due to long half-life and more branching ratio ^{226}Ra is the most important. ^{226}Ra, a daughter of Uranium series having been extracted and concentrated for various industrial, commercial, medical and educational activities. An important decay product of

^{226}Ra is ^{222}Rn most harmful gas present in the environment. An adult contain 1 Bq of ^{226}Ra, with greatest concentration in bones. Most of the burden of radium is found in the skeleton.

Fertilizers play vital role in agriculture, especially phosphate containing fertilizers have become essential to the world's agriculture. They are used worldwide in increasing quantities as a substitute of natural nutrients essential for the growth of various crops and other plants. Fertilizers used in Pakistan have two main sources: domestic production and imports. Locally available fertilizers are manufactured in various factories of Pakistan. However, some of the phosphatic fertilizers are imported from other countries of the world.

It has been known since early in this century that phosphate rocks contain substantial concentration of uranium, thorium and radium and radium decay products (Beretka & Methew, 1985). Since phosphate rock is an important raw material used for the manufacturing of different types of phosphatic fertilizers, therefore, when this rock is processed into phosphatic fertilizer most of the uranium and some of the radium accompanies the fertilizer. It has also been estimated earlier that phosphatic fertilizers applied to the fields in recommended amounts could raise the local exposure rates by about 0.5 mR/hr and run off from fertilized fields may substantially increase radioactivity levels in surface water (Guimond & Harden, 1989). Moreover, phosphatic fertilizers stored in enclosed warehouses can also lead to elevated radon levels. Thus potential radiological hazards resulting from direct exposure, surface run-off, inhalation and ingestion of food grown with fertilizers cannot be ignored (Linsalta, 1989).

This work is a continuation of our ongoing study on various building materials and a variety of samples from environmental media and published elsewhere (Khan et al., 1992; 1994; 1995; 1997; 1998; 2001; 2002). In the present study different brands of locally available as well as imported fertilizers and samples of phosphate rock were analyzed for their gamma emitters and the results were also compared with the data available for other countries of the world.

EXPERIMENTAL

Sample collection and preparation

Domestic fertilizer samples, were collected mostly from fertilizer factories and regional offices of the National Fertilizer Development Centre (NFDC). The imported fertilizers were obtained from Fertilizer Import Development Centre (FIDC), Lahore and from Marketing Division of the National Fertilizer Corporation (NFC), Islamabad. The phosphate rock samples were mostly collected from Hazara Phosphate rock deposits. The samples were packed in radon impermeable plastic containers. The geometrical dimensions of fertilizer samples were kept identical to those of reference material (RG-set and Soil-6) obtained from the International Atomic Energy Agency (IAEA). These reference materials were used to calibrate the gamma ray spectrophotometer. The samples and reference materials were stored for more than 40 days to attain equilibrium amongst ^{226}Ra and its short-lived decay products.

Radiometric measurement

Radiometric measurement was performed using a high purity germanium detector. The emphasis was on the determination of specific activity concentration of ^{226}Ra, ^{232}Th and ^{40}K. Every sample of phosphatic fertilizer was measured for 40,000 seconds and its spectrum was stored in a PC-based multichannel analyser (MCA). After counting for the specified time, the gamma-ray spectra were automatically calculated with the help of Intergamma software (Intertechnique, France) and loaded in the PC-based MCA. The analysis of ^{40}K was based upon its single peak, whereas the analysis of ^{226}Ra and ^{232}Th depended upon the peaks of the daughter products in equilibrium with their parent nuclides.

RESULTS AND DICUSSION

The three long-lived naturally occurring radionuclides i.e. ^{226}Ra, ^{232}Th and ^{40}K are commonly known as primordial radionuclides. They are basically associated with the creation of earth and are normally found in the earth crust. They normally enter the human body through inhalation and ingestion and accumulate in critical organs, where they deliver radiation doses. ^{226}Ra usually accumulates in human bones and skeleton tissues, ^{232}Th in lungs, liver and skeleton and ^{40}K in muscles. The radiation damage and radiobiological changes produced by these radionuclides include weakening of immune systems and development of different types of diseases, mostly cancers.

Results of five different types of fertilizers and phosphate rock samples are shown in Table 1 along with minimum, maximum and average values of the activities due to ^{226}Ra, ^{232}Th and ^{40}K. The table shows that the average values of the specific gamma activities due to ^{40}K for di-ammonium phosphate were greater than the rest of the phosphatic fertilizers, while in case of ^{226}Ra and ^{232}Th their average specific activities were found larger in mono-ammonium phosphate fertilizer samples as compared to other phosphatic fertilizers. However, it is obvious from this table that the concentration of ^{226}Ra in all the phosphatic fertilizers as well as phosphate rock samples is much higher than ^{232}Th and ^{40}K. This is due to larger uranium deposits in the earth crust and consequently in the phosphate rock, being used for the manufacturing of phosphatic fertilizers. Table 2 lists a comparison of specific activities due to all the three detected radionuclides in single superphosphate fertilizer samples with some of the data available in the literature for other countries of the world. The table shows that the specific activity due to ^{226}Ra in single superphosphate samples of Pakistan is approximately equal to that of Germany. However, the fertilizers from Finland and USA show much lower and higher contents of ^{226}Ra respectively, as compared to that of Pakistan. The specific activity of ^{232}Th in single superphosphate fertilizers available in Pakistan is approximately equal to that of USA but the fertilizers from Finland and Germany show much lower concentration as compared to that of Pakistan. In case of ^{40}K the Pakistani samples showed lower values of specific activity than other countries cited in Table 2.

In order to represent the specific activities due to ^{226}Ra, ^{232}Th and ^{40}K by a single quantity, which takes in to account the radiation hazards associated with them, a common index has been introduced and is called radium equivalent activity (Ra_{eq}) and is mathematically defined as[11]:

$$Ra_{eq} = A_{Ra} + 1.43 \times A_{Th} + 0.077 \times A_K \quad (1)$$

Where A_{Ra}, A_{Th} and A_K are the specific activities of ^{226}Ra, ^{232}Th and ^{40}K respectively. It may be noted that ^{238}U has been replaced with the decay product ^{226}Ra because there may be a disequilibrium between ^{238}U and ^{226}Ra. While defining Ra_{eq} activity according to equation (1), it has been assumed that 10 Bq of ^{226}Ra, 7 Bq of ^{232}Th and 130 Bq of ^{40}K produce the same gamma doses. The Ra_{eq} is related to the external gamma radiation dose and the internal dose due to radon and its daughters. The calculated values of Ra_{eq} activities are presented in Table 3. These values can now be used to determine the concentration of radioactivity being spread along with the fertilizer in the agricultural fields if the quantity of fertilizer used is known. In Pakistan there is a large variation in the quantity of fertilizer used. It depends upon the type of crop and the area of its cultivation i.e. Irrigated or Barani. Thus, the quantity of radioactivity being spread will vary from area to area and crop to crop. However, since now the basic information is available therefore the amount of radioactivity can easily be calculated. It has been observed that the radium content in all the phosphatic fertilizers, analysed in the present work, are very high, therefore, this may result in external hazards to the manufacturer of fertilizers. Moreover, if these fertilizers are stored in places with poor ventilation system, then radon buildup may also result in a significant hazards to workers.

TABLE 1. SPECIFIC GAMMA-RAY ACTIVITIES DUE TO ^{40}K, ^{226}RA AND ^{232}TH IN DIFFERENT BRANDS OF PHOSPHATIC FERTILIZERS AVAILABLE IN PAKISTAN

Fertilizer	No. of Samples	Specific gamma-activities (Bq.kg^{-1})		
		^{40}K	^{226}Ra	^{232}Th
Single Superphosphate	20			
Minimum		95.2	499.1	26.5
Maximum		331.4	611.4	203.4
Average		221.2	556.3	49.7
Triple Superphosphate	25			
Minimum		90.9	514.4	57.3
Maximum		164.6	612.5	96.1
Average		142.5	558.6	84.8
Nitrophos	20			
Minimum		129.6	307.7	14.8
Maximum		298.1	501.2	162.9
Average		205.7	389.4	79.9
Mono Ammonium Phosphate	20			
Minimum		91.2	515.1	75.1
Maximum		167.8	619.6	97.5
Average		137.7	560.9	85.1
Di Ammonium Phosphate	20			
Minimum		96.9	490.5	27.9
Maximum		329.2	578.4	197.7
Average		237.5	545.3	65.5
Phosphate Rock	50			
Minimum		103.5	416.3	18.6
Maximum		359.8	520.7	112.1
Average		207.3	439.5	50.4

TABLE 2. COMPARISON OF THE SPECIFIC ACTIVITIES OF SINGLE SUPERPHOSPHATE FERTILIZERS AVAILABLE IN PAKISTAN AND OTHER COUNTRIES OF THE WORLD

Country	^{40}K	^{226}Ra	^{232}Th	Reference No.
Finland	3200	54	11	(Mustonen, 1985)
USA	200	780	49	(Guimond and Harden, 1989)
Germany	720	520	15	(Pfister et al., 1976)
Pakistan	221	526	50	Present work

TABLE 3. ESTIMATED VALUES OF RA_{eq} ACTIVITIES IN DIFFERENT BRANDS OF PHOSPHATIC FERTILIZERS AVAILABLE IN PAKISTAN

Fertilizer	Ra_{eq} activities ($Bq.kg^{-1}$)		
	Min	Max	Ave
Single superphosphate	544.3	929.8	644.4
Triple superphosphate	603.0	667.6	690.8
Nitrophos	338.8	757.1	519.5
Mono ammonium phosphate	629.5	771.9	693.2
Di ammonium phosphate	537.9	886.5	657.3

CONCLUSIONS

All the phosphatic fertilizers and phosphate rock samples have shown higher amount of ^{226}Ra and it was found to vary from 307.7 $Bq.kg^{-1}$ to 617.5 $Bq.kg^{-1}$, because of larger deposits of uranium in the earth crust and consequently in phosphate rock, being used as a main raw material for the manufacturing of phosphatic fertilizers. This can result in significant radiation exposure if these fertilizers are handled in places with poor ventilation that could lead to radon accumulation.

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