

Hazard of NORM from phosphorite of Pakistan

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ABSTRACT

In order to investigate the radiological hazard of naturally occurring radioactive material (NORM) in phosphorite deposits of Pakistan, 26 samples of phosphorite were collected from the phosphorite mines near Abbottabad, and 20 samples of single superphosphate (SSP) fertilizer were obtained from the warehouses in Pakistan. Activity concentration in all the samples was assayed using HPGe detection system. Specific activity values of ^{238}U , ^{40}K , ^{226}Ra and ^{232}Th in the samples of phosphorite were 550 ± 156 (329–845), 206 ± 72 (93–362), 511 ± 189 (316–830) and 52 ± 17 (23–81) Bq kg^{-1} , respectively; and those in SSP fertilizer due to these radionuclides were 637 ± 44 (596–687), 164 ± 24 (113–215), 589 ± 44 (521–671) and 29 ± 6 (16–45) Bq kg^{-1} , respectively. The results were compared with that of worldwide soil. Outdoor external dose rate due to gamma rays from phosphorite was calculated to be 276 ± 94 (177–441) nGy h^{-1} and external dose rate in a room made of phosphorite containing material was estimated to be 706 ± 243 (455–1129) nGy h^{-1} . The concentration of radon was measured in phosphorite mines and in the warehouses for SSP fertilizer by an active method. Protective measures have been proposed to control the pollution in the phosphorite mining and processing, and fertilizer storage areas.

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1. Introduction

NORM stands for naturally occurring radioactive materials, which may contain any of the primordial radionuclides or radioactive elements as they occur in nature, such as uranium, thorium, their radioactive decay products, and potassium that are disturbed in the earth's crust in variable amounts [1]. Radiation levels presented by NORM are generally referred to as a component of “natural background radiation”. Natural uranium can substitute calcium in the phosphate rock (PR) structure due to similarity in ionic sizes between U^{4+} and Ca^{2+} , PR contains additional NORM due to uranium and its progeny [2].

Phosphorus (P) does not occur free in nature but its compounds are widely distributed, mainly as phosphates, and are found in many rocks and minerals. There are over 150 species of phosphate minerals of which the most common are apatite, phosphorite, wavellite and vivianite [3]. The phosphate ores that are in the form of calcium phosphates [$\text{Ca}_3(\text{PO}_4)_2$] are called phosphorites or apatites depending on origin of the ore. Phosphorites are very old marine sedimentary deposits associated with fossils while apatites are of igneous origin formed in situ [4]. Phosphorites are widely used as a raw material for the production of phosphate fertilizer (PF). In Pakistan, single super phosphate (SSP) fertilizer is manufactured from phosphorite. Hazara phosphorites are the only known

PR deposits in Pakistan. High-grade ore reserves of this area are being exploited for the manufacturing of SSP at Haripur and Jaranwala Fertilizer Plants in Pakistan [5]. Low-grade phosphate ore is used for manufacturing of feed for poultry and life stock. The impurities and contaminants in phosphorite are transferred to the fertilizer and feed made of it.

Phosphate make chemical complexes with uranium, therefore PR contains radioactivity of uranium and its progeny [6]. The high concentration of NORM is a source of radiological hazard that may cause significant exposure to radiation of people working in various phosphate industrial operations and of general public living in the premises of PR deposits. Radon gas emanates from the NORM in PR; and accumulates in caves, mines, houses made of/on PR, and in PF warehouses. Radon progeny can be a cause of lung cancer for the population exposed to high concentration of radon.

Human beings are exposed directly or indirectly to radiation of NORM in PR and PF. NORM can reach humans via several pathways, including the food chain, inhalation or ingestion of airborne radioactive dust and the inhalation of radon isotopes and their progeny, which reach the atmosphere as a result of the exhalation of radon isotopes from the ground surface or from the surface of building materials [7]. NORM is the source of background terrestrial radiation that varies from place to place depending on where one lives. Ingestion and inhalation of NORM can be a source of deleterious effects of ionizing radiation.

The purpose of present study was to determine the level of NORM in the phosphorite of Pakistan and in the fertilizers derived from it; therefore, radioactivity was measured in the samples of PR

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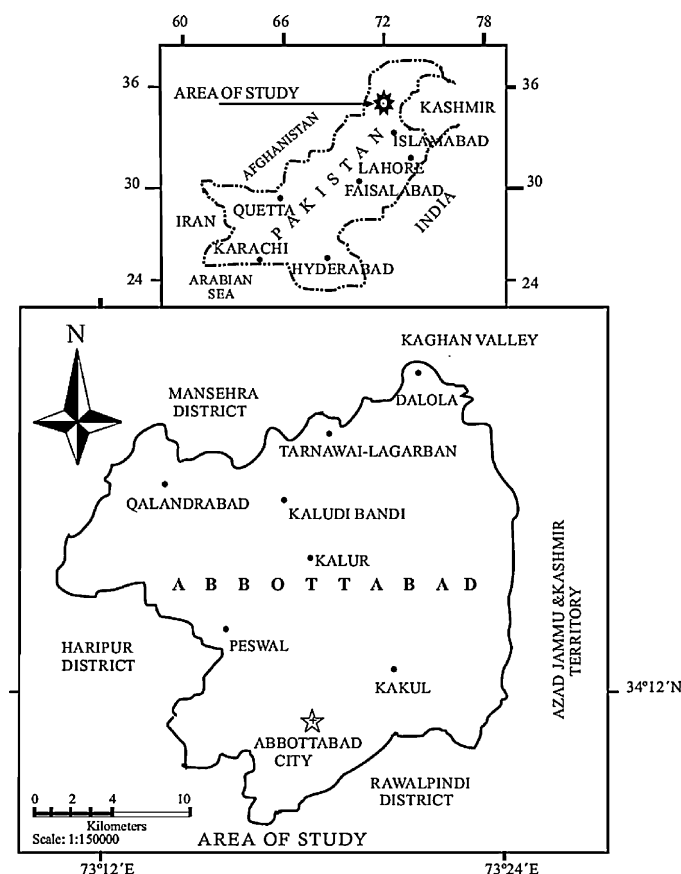


Fig. 1. Location of phosphorite sampling sites in the area under study.

collected from the mines in Hazara division and in the SSP fertilizer manufactured from this rock in Pakistan. The most widely used technique of gamma ray spectrometry based on HPGe (high purity germanium) detector was employed. The amount of radioactivity in the study area was compared with the data compiled from literature for PR and PF of some counties of the world. Radiological hazard was assessed in terms of radiation dose from the PR and radon emanating in the phosphorite mines in the study area.

2. Material and methods

2.1. Study area

The deposits of phosphate belong to the sedimentary rock formations that occur in Hazara division in the North West Frontier Province (NWFP) of Pakistan. These are the only economical deposits of phosphate in the country. Majority of phosphorite deposits of this region exist in an area of about 30 km² in linear dimension within latitudes 34°5' to 34°30'N and longitudes 73°15' to 73°20'E. The area includes Kakul, Kalur, Kakul West, Lambidogi, Tarnawai, Kaludi-Bandi, Guldanian, Dalola and many other localities in a belt near Abbottabad city in Hazara division of Pakistan. It is about 3819 feet above sea level. The study area is shown in Fig. 1. The range of P₂O₅ content in these sites is 25–30% [8]. Around 750,000 tons of PR of acceptable quality is available at Kakul mine alone [9].

2.2. Sample management

The sampling of PR was carried out from: (a) the open pit and underground mines of Kakul, (b) the open pit mine of Lambidogi, and (c) the rock crushing and milling plant of Sarhad Development

Authority (SDA) at Kakul near Abbottabad in the NWFP, Pakistan. Phosphorite samples were collected from various sections of each mine including hanging wall (formation immediate above the main phosphorite body), main phosphorite formation, and footwall (formation immediate below the main phosphorite body). A total of 26 samples were collected: 20 samples from various sections of different mines, and 6 from PR crushing plant near Kakul. Each sample was a representative of 5 specimens; one specimen was collected from the central specified site, and the others were obtained from the 4 peripheral locations around the central point [10]. The rock specimens were crushed to small pieces and mixed uniformly.

The phosphorite of Hazara deposit is mainly used for the manufacture of SSP fertilizers in Pakistan. The samples of SSP fertilizer were collected from (a) the fertilizer plants at Haripur and Jaranwala in Pakistan, and (b) the fertilizer warehouses in various cities of Pakistan. The samples from fertilizer factories were consisted of the mixtures of specimens of different batches, and those from the warehouses were the mixtures of the specimens collected from various sites. A sample was a mixture of at least 4 specimens uniformly mixed. The samples of SSP fertilizer, 20 in number, were assembled for this study.

Around one kg each of PR and PF sample was put into the cloth bag with proper marking. The samples were shifted to Geochemistry Laboratory of Pakistan Institute of Engineering and Applied Sciences (PIEAS). The rock samples were washed to remove soil dust and dried in the sun. The rock and fertilizer samples were blended and ground to make powder. The powder was heated at 100 °C for more than 20 h to remove moisture if any and passed through a sieve of mesh size 200 μm.

Reference material RG1 set was obtained from Analytical Quality Control Services (AQCS) of International Atomic Energy Agency (IAEA) for calibration of gamma ray spectrometer. The RG1 set consisted of uranium, thorium, and potassium with certified concentration of these elements. The samples and reference material were sealed in radon impermeable plastic containers of dimensions: thickness 2 mm, diameter 65 mm and height 75 mm. Density of the study samples and that of reference material were kept identical in packing containers. The samples and the reference material were stored for 40 days to achieve secular equilibrium between ²²⁶Ra and ²²²Rn. The details regarding sample management are given elsewhere [11–13].

2.3. Radiometric assay

Specific activity measurement of the NORM in the samples of PR and PF were performed in the Low Level Activity Measurement (LLAM) laboratory of PIEAS. The assay of the samples was carried out with a gamma ray spectrometry system consisting of a high purity germanium (HPGe) detector coupled with a PC-based multichannel analyzer (MCA) along with APTEC software installed in the PC. The detector was kept in a 30 cm × 30 cm × 30 cm cavity shielded with 10 cm lead with 2 mm each successive inner lining of Cu, Al and Perspex to reduce background in gamma ray spectra [12]. Head of the detector was placed nearly at the centre of the cavity. Energy calibration of the system was done initially with ²⁴¹Am, ⁵⁷Co, ¹³⁷Cs, ²²Na and ⁶⁰Co gamma ray point sources and subsequently with the reference materials. Resolution (FWHM) of the system was 1.9 keV at 1332.5 keV gamma peak of ⁶⁰Co point source kept at a distance of 25 cm in front of the detector face.

Efficiency calibration of the detection system was performed by using the reference material RG1 set. Efficiency vs. energy curve was produced from the spectra of reference materials and a polynomial was fitted to the efficiency curve that was stored in the PC. Specific activities (activity mass concentrations) of ⁴⁰K, ²²⁶Ra and ²³²Th were determined in the samples of PR and PF under study. The details regarding efficiency calibration and activity measure-

Table 1

The concentration of NORM in phosphorite from some mines in the vicinity of Abbottabad in NWFP, Pakistan.

Location	No. of samples	NORM concentration (Bq kg ⁻¹)			
		⁴⁰ K	²²⁶ Ra	²³² Th	²³⁸ U
Rock					
Footwall and hanging wall	6	176 ± 60 (102–251)	59 ± 9 (48–72)	38 ± 9 (31–46)	62 ± 11 (51–75)
Phosphorite					
Open pit mine, Lambidogi	5	127 ± 29 (93–171)	352 ± 10 (337–365)	40 ± 17 (23–68)	461 ± 123 (339–573)
Underground mine, Kakul	4	212 ± 18 (189–233)	744 ± 123 (563–830)	68 ± 11 (54–81)	771 ± 127 (576–845)
Open pit mine, Kakul West	5	209 ± 52 (166–278)	494 ± 158 (348–758)	44 ± 12 (36–64)	502 ± 167 (355–673)
Phosphorite Crushing plant, Kakul	6	266 ± 79 (179–362)	503 ± 196 (316–776)	57 ± 13 (39–80)	518 ± 205 (329–781)
Average range	20	206 ± 72 (93–362)	511 ± 189 (316–830)	52 ± 17 (23–81)	550 ± 156 (329–845)

Table 2Activity concentration and external dose rate levels of ⁴⁰K, ²²⁶Ra and ²³²Th from soil of various countries of the world (UNSCEAR [20]).

Radionuclide	Activity concentration (Bq kg ⁻¹)			External dose (nGy h ⁻¹)		
	Median	Minimum	Maximum	Median	Minimum	Maximum
⁴⁰ K	400	140	850	17	6	35
²²⁶ Ra	35	17	60	16	8	28
²³² Th	30	11	64	18	7	39
²³⁸ U	35	16	110			
Total				51	21	102

ments are given somewhere else [14–17]. Radiological hazard was assessed based on the measured specific activity values. Annual effective external dose was calculated for phosphorite rock and PR made rooms.

2.4. Radon measurement

For the measurement of radon concentration in phosphorite mines and fertilizer warehouses, an active method was applied. The radon monitor consisted of a portable “Alpha Guard PQ 2000 PRO” which has an ionization chamber of active volume 0.56 L. Radon measuring range of this detector is 2–20,000 Bq m⁻³ [18]. Radon concentration was measured inside and outside of the phosphorite mines at Peswal Village and Banda Pir Khan; and in the fertilizer warehouses of four districts of the Punjab province of Pakistan. Based on the measured concentration of radon, annual effective dose was calculated for mining and warehouses environments.

3. Results and discussion

3.1. Phosphorite

Activity concentrations of NORM measured in the samples of the phosphorite and rocks in the hanging and foot walls of the PR are given in Table 1. The worldwide background activity concentration levels of ⁴⁰K, ²²⁶Ra, ²³²Th and ²³⁸U in soil from various countries of the world have been compiled in the UNSCEAR 2000 report; the range and the median values of these radionuclides are represented in Table 2. To compare the level of activity mass concentrations of ⁴⁰K, ²²⁶Ra, ²³²Th and ²³⁸U in PR of present study with that measured worldwide; we have compiled data from literature and represented in Table 3. The weighted average of activity concentrations of the radionuclides in the phosphorite samples was determined and considered as the representative level of NORM in PR for Pakistan. The average value and the range of activity mass concentrations for Pakistan are given in Table 3.

The values of measured activity concentration of ⁴⁰K varied from place to place in the samples of phosphorite and had no clear-cut boundary between those in the rock samples of hanging and foot walls. Activity concentration values of ⁴⁰K are comparable to the

natural background level for this radionuclide in the earth's crust. The values lie within the range of this radionuclide given in Table 2. Specific activity of ⁴⁰K in PR of 22 places of the world is given in Table 3. Five places are at higher level and 17 places show lower value of this nuclide than that in Pakistani phosphorite.

The measured value of specific activity of ²³²Th in the phosphorite samples is relatively higher than that in the samples of hanging and foot walls. The samples of underground mines have even more value of this radionuclide in phosphorite. While comparing the activity concentration values of ²³²Th in the studied samples with that in the worldwide soil, it can be seen that the samples of phosphorite contain average concentrations relatively higher than the median value of this radionuclide given in Table 2. Among the 26 places of the world given in Table 3, activity concentration of ²³²Th in PR of 7 places is higher and that of 19 places is lower than that in phosphorite of Pakistan.

As given in Table 1, the concentration values of ²²⁶Ra are relatively higher than those for ⁴⁰K and ²³²Th in the phosphorite of study area. Specific activity of ²²⁶Ra in the main rock body of phosphorite is larger than that in the hanging and foot walls of the open pit and underground mines. Hanging and foot walls of underground mine are composed of limestone and chert respectively, and both of the open pit mines belong to dolomite. Limestone, chert and dolomite are not prone to uranium; therefore, the activity mass concentration of ²²⁶Ra in these formations is quite lower than that in the phosphorite samples but is higher than the median background activity level of soil given in Table 2. Hanging and foot walls are not a part of PR, therefore, activity mass concentrations of the samples from these sections are not taken into account for further discussion. After excluding the activity concentrations of the samples of hanging and footwalls, the results of 20 samples of phosphorite were of significance from radioactivity point of view. Specific activity of ²²⁶Ra varied between 316 and 830 Bq kg⁻¹ in these 20 samples.

As far as comparison of ²²⁶Ra in PR of various places of the world is concerned, its activity concentration levels are extremely higher than the background activity level of this radionuclide given in Table 2. Activity concentration values of ²²⁶Ra as given in Table 3 for various countries of the world vary from country to country and region to region even within same country. The phosphorite

Table 3Specific activity of ^{40}K , ^{226}Ra and ^{232}Th in PR from various locations of the world.

Country/location	Activity mass concentration (Bq kg^{-1})				References
	^{238}U	^{40}K	^{226}Ra	^{232}Th	
Algeria	1627	22	619	64	[25]
Brazil	1313	1202	256	3238	[2]
China	150		150	25	[26]
Egypt/Abu-Tartor	408	21.4	287	23.7	[27]
Egypt/Abu-Zaabal	523	19	514	37	[28]
Finland		110	10	10	[29]
Israel	1726	4	1852	11	[25]
Jordan	1837	8	1044	2	[25]
Russia/Kola	40	40	30	80	[30]
Morocco	1700	10	1700	30	[31]
Morocco	1700	10	1600	20	[30]
Nigeria/Sokoto		40	558	16	[32]
Saudi Arabia	519	250	—	40	[33]
South Africa	1300	4	1100	30	[30]
South Korea		49	355	4	[1]
Sudan/Kurun	684	23	555	0.83	[34]
Sudan/Uro	2598	52	2263	3	[34]
Tanzania/Arusha	4641	286	5022	717	[35]
Tanzania/Arusha		280	5760	350	[36]
Tiba Togo	1300	4	1100	30	[30]
Togo/Hahatoe			968	90	[32]
Tunisia	580	32	821	29	[25]
Turkey	557	256	625	26	[37]
USA/California Southern	4800		4800	78	[26]
USA/Florida Central	1500		1600	16	[26]
USA/Florida Northern	474		648		[38]
W. Sahara/Bu–Croa	900	30	900	7	[30]
Pakistan/Hazara	550 ± 156 (329–845)	206 ± 72 (93–362)	511 ± 189 (316–830)	52 ± 17 (23–81)	Present study

deposits of Pakistan contain lesser specific activity of ^{226}Ra than the phosphate deposits of 20 places of the world. There are 6 places where activity level of this nuclide is lower than that in Pakistani phosphorite.

As far as the ratio of ^{226}Ra to ^{232}Th is concerned, it is normally less than unity when background activity of the earth's crust is considered [19]. The results of present study indicate that activity of ^{226}Ra dominates that of ^{232}Th . The ratio varies between 5 and 17 with an average value of 10.4 ± 3.5 . Elevated concentration of ^{226}Ra in the samples is due to the presence of uranium, as ^{226}Ra is a daughter product in ^{238}U decay series.

The concentration of ^{238}U as given in Table 1 is slightly higher than that of ^{226}Ra , which follows the similar trend as shown in Table 3 for most of the countries of the world. When compared with the worldwide data, the concentration of ^{238}U in the phosphorite of Pakistan is higher than that of 6 places and lower than that of 16 places of the world. The concentration of ^{238}U in the worldwide phosphate varies in a wide range from 40 to 4800 Bq kg^{-1} .

In order to find the extent of the existence of these radioactive nuclides together at a particular place, correlation studies were performed between the combinations of radionuclides. The correlations coefficients for ^{226}Ra – ^{40}K , ^{232}Th – ^{40}K , and ^{226}Ra – ^{232}Th were computed for 20 phosphorite samples, which vary between 0.79 and 0.92 that show the strong correlations among the radionuclides. The strong correlations between the activities indicate that the individual result for any one of the radionuclide concentration in each pair is a good predictor of the concentration of the other and they belong to same source. The correlation coefficient

for the relation ^{226}Ra – ^{238}U was 0.97, which predicts that both the radionuclides belong to same source and have close association of each other. A matrix showing the correlation coefficients is given in Table 4.

Uranium and its decay products emit various ionizing radiations such as alpha and beta particles, and gamma rays. The health impacts of ionizing radiation even at low doses include the increase of various types of cancers, genomic instability, life-shortening and negative impacts on all the body functions.

3.2. SSP fertilizer

Single superphosphate (SSP) fertilizer is formed by mixing PR with sulphuric acid. The reaction product is dried along with all the contaminants in PR and sulphuric acid. The jumble is ground to powder at Jaranwala fertilizer factory and converted to granules at Hazara fertilizer factory in Pakistan. Phosphate (P_2O_5) grade of the Pakistani phosphorite is low with high concentration of SiO_2 . The grade is improved by combining the local phosphorite with the PR imported from Jordan and Egypt. The activity concentration in the SSP fertilizers manufactured in Pakistan depends upon that in the PR of Egypt, Jordan and Pakistan and the concentrations of the radionuclides of concern in PR of these countries are given in Table 3.

The concentrations of the radionuclides measured in the SSP fertilizer produced in Pakistan are given in Table 5. The concentration levels of all the radionuclides in the SSP fertilizer of both the factories are almost similar within statistical error. The concentrations of ^{40}K and ^{232}Th in SSP fertilizer are lower than that of phosphorite of Pakistan; this may be due to lower value of these radionuclides in the PR of Jordan and Egypt than that in PR of Pakistan. The activity concentration of ^{226}Ra in the fertilizer is higher than that of the phosphorite of Pakistan; this is because of higher values of this radionuclide in the PR of Jordan and Egypt. The elevated concentration of NORM in SSP fertilizer is one of the sources of radioactive contamination of agricultural fields, the crops grown

Table 4

Correlation coefficients of various radionuclide relations.

	^{40}K	^{226}Ra	^{232}Th	^{238}U
^{40}K	1	0.79	0.87	0.77
^{226}Ra		1	0.92	0.97
^{232}Th			1	0.89
^{238}U				1

Table 5Activity concentration of ^{40}K , ^{226}Ra and ^{232}Th in SSP fertilizer produced in Pakistan.

Sample identity	Activity mass concentration (Bq kg^{-1})			
	^{40}K	^{226}Ra	^{232}Th	^{238}U
Hazara phosphate fertilizers (10 samples)				
Minimum	113 \pm 12	521 \pm 26	23 \pm 6	623 \pm 32
Maximum	135 \pm 15	638 \pm 29	45 \pm 7	687 \pm 34
Mean	121 \pm 17	606 \pm 31	35 \pm 6	658 \pm 45
Jaranwala phosphate fertilizer (10 samples)				
Minimum	193 \pm 14	540 \pm 27	16 \pm 5	596 \pm 34
Maximum	215 \pm 16	671 \pm 29	31 \pm 6	641 \pm 36
Mean	207 \pm 21	572 \pm 32	23 \pm 6	616 \pm 47

in these fields, and surface water ponds. There is direct or indirect exposure of human beings to this source of pollution.

Specific activity concentration values of the NORM in SSP fertilizer for some of the countries of the world were compiled from literature and are represented in Table 6. The weighted average activity concentration of 20 SSP fertilizer samples was determined as a representative value for Pakistan and is also given in Table 6. The distribution of activity concentration of primordial radionuclides in SSP fertilizer from some countries of the world varies from country to country.

3.3. Radiological hazard

The humans living and working in the study area are affected from the radiological hazard of NORM in the PR by various means. The laborers involved in mining, milling and processing of PR are exposed internally and externally to NORM in addition to other industrial hazards. General public not related to phosphate industry but living and working in the vicinity of the radioactive area are influenced from NORM containing dust. The inhabitants living in the dwellings made of materials belonging to PR, made on PR beneath foundations, or living in PR residue filling houses are exposed to radon and gamma radiation. The application of NORM containing PF into agricultural fields can be a direct or indirect and an internal or external source of exposure of human beings to radiation.

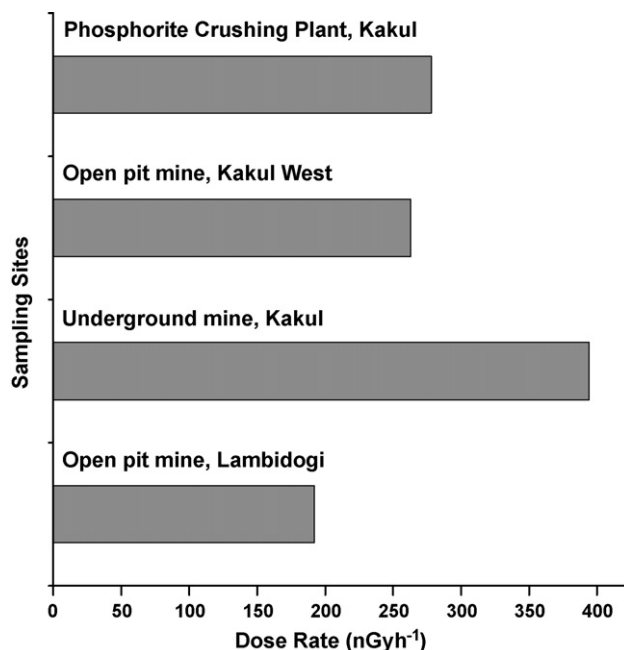
Radiological hazard is assessed by a single index taking into account the measured activity concentration of ^{40}K , ^{226}Ra and ^{232}Th . Radiologic hazard can be estimated through various criteria [10–17]. In the present study, the level of hazard has been estimated in terms of outdoor and indoor external dose rates. Based on the calculated dose rate values, annual effective dose was determined for the mineworkers and house dwellers of the study area.

3.4. Outdoor external dose

The radiological hazard of the PR was estimated through radiation dose delivered by the radionuclides of NORM in the rock.

Table 6Activity concentration of ^{40}K , ^{226}Ra and ^{232}Th in SSP fertilizer from various countries of the world.

Country	No. of samples	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	References
Bangladesh	1	142.7 \pm 14.2	291.7 \pm 14.8	15.6 \pm 3.3	[39]
Brazil	1	375 \pm 26	871 \pm 44	100 \pm 7	[40]
Brazil	3		246 \pm 40 (1.3–879)	256 \pm 49 (81–546)	[41]
Brazil		<5	304	286	[42]
Brazil		<5	262	272	[42]
Egypt	3	8.2 \pm 2.2 (2.1–13.6)	627 \pm 24 (516–704)	6.1 \pm 2.4 (1.3–9.1)	[43]
Finland		3200	54	11	[29]
Germany		720	520	15	[44]
Lebanon		4.1 \pm 0.3	1043 \pm 25		[45]
USA		200	780	49	[46]
Pakistan	20	164 \pm 24	589 \pm 44	29 \pm 6	Present study

**Fig. 2.** External dose rate variations at sampling sites.

Assuming that radionuclides ^{40}K , ^{226}Ra and ^{232}Th are uniformly distributed in a PR slab of semi-infinite thickness, gamma dose rate at a distance of one meter above the surface of the slab can be calculated using the following relation [20]:

$$\dot{D} = 0.0417A_K + 0.462A_{Ra} + 0.604A_{Th} \quad (1)$$

where A_K , A_{Ra} and A_{Th} are respectively the activity mass concentrations (in Bq kg^{-1}) of ^{40}K , ^{226}Ra and ^{232}Th in the sampling sites. External dose rate was estimated for 20 sampling locations in the study area of phosphorite deposit. The variations in dose rate at phosphorite sites are shown in Fig. 2. The dose rate varied from 177 to 441 nGy h^{-1} with an average value of $276 \pm 94 \text{ nGy h}^{-1}$. The minimum value of the derived dose rate is about 70% greater than the maximum value of the world's soil background level of 102 nGy h^{-1} as given in Table 2, which indicates the intensity of hazard level in the area under study.

3.5. Indoor external dose

For the estimation of indoors external dose, it is assumed that a room is made of material containing PR. Similar to the external dose outdoors; various models have been developed for the external dose indoors. Indoor external dose in a room of dimensions $2.8 \text{ m} \times 4 \text{ m} \times 5 \text{ m}$, wall density 2.35 g cm^{-3} , and wall thickness

Table 7

Indoor and outdoor radon concentration from two mining places of phosphorite of Pakistan.

Area	Radon concentration (Bq m ⁻³)	
	Mine inside	Mine outside
Peswal village, cave like mine	215 ± 51	56 ± 30
Peswal village, ventilated mine	100 ± 39	43 ± 19
Banda Phir Khan (F-Zone)	96 ± 39	34 ± 30

Table 8

Radon concentration level and annual mean effective dose in the warehouses for fertilizer.

District	Concentration (Bq m ⁻³)	Effective dose (mSv y ⁻¹)
Sialkot/Daska	44.64 (36.97–52.53)	0.49 (0.41–0.58)
Gujranwala	35.00 (19.02–51.74)	0.39 (0.21–0.57)
Gujrat	31.27 (17.12–40.55)	0.35 (0.19–0.45)
Sheikhupura	22.05 (20.2–24.06)	0.24 (0.22–0.27)

20 cm was calculated using the following relation [21]:

$$\dot{D} = 0.10A_K + 1.21A_{Ra} + 1.29A_{Th} \quad (2)$$

where A_K , A_{Ra} and A_{Th} are respectively the activity mass concentrations (in Bq kg⁻¹) of ⁴⁰K, ²²⁶Ra and ²³²Th in the construction materials. External dose rate for the indoor environment was also estimated for rooms made of PR in the study area of phosphorite deposit. The dose rate varied from 455 to 1129 nGy h⁻¹ with an average value of 706 ± 243 nGy h⁻¹. The minimum value of the derived dose rate is approximately 4.5 times greater than the maximum value of the world's soil background level of 102 nGy h⁻¹ as given in Table 2, which presents the severity of hazard level due to phosphorite in the study area.

3.6. Radon exposure

Radon concentration was measured in two phosphorite mines in the area under study and in four warehouses where SSP fertilizer is kept for some interim period.

3.6.1. Exposure of miners

For assessment of radon exposure from PR, radon concentration was measured inside and outside of two phosphorite mines in vicinity of Abbottabad city in Pakistan. The concentration of radon is given in Table 7. The contrast in the inside and outside values of radon concentration is quite obvious. Values for temperature and humidity level varies from (30–33)°C and (32–39)% (inside the mine) to (31–34)°C and (28–39)% (outside the mine). While air pressure remains 877 mbar in all the studied sites. The measured concentration was compared with the permissible level of radon in the uranium mines, i.e. 75 Bq m⁻³ [22]. The values of measured radon concentration in the mines are approximately 1.3–2.9 times greater than the permissible value; the risk of radon-induced detrimental effects is obviously high for the mineworkers.

3.6.2. Exposure of warehouse workers

In order to evaluate the exposure of warehouse workers to radon, its concentration was measured in fertilizer warehouses of four districts in the Punjab province of Pakistan. The concentration of radon in all the four studied warehouses is presented in Table 8. Five sites were selected for radon measurement in a warehouse and the representative concentration of radon in a warehouse was the average of all the concentrations measured at these sites. According to occupational safety and health association (OSHA), radon level for mitigation is 148 Bq m⁻³ [23], which is equal to that of the US EPA's residential acceptable level of radon. If level of radon is compared with the permissible level in houses, it is clear that fertilizer

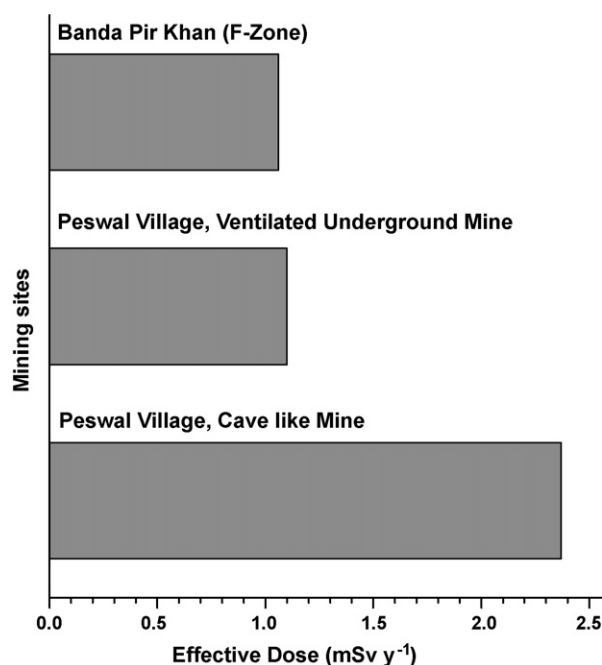


Fig. 3. Annual mean effective dose for phosphate mines.

warehouses contain radon within the acceptable range causing no much harm to the workers.

3.7. Effective dose

3.7.1. Gamma dose

Annual effective dose from external exposure to gamma rays emitted from PR can be determined using the following relation [24]:

$$E = \dot{D} \times V \times T \times O \times 10^{-6} \quad (3)$$

where E is the annual effective dose (mSv y⁻¹), \dot{D} is the dose rate (nGy h⁻¹), V is the absorbed to effective dose conversion factor (0.7 Sv per Gy), T hours per year (8760 h), O is the occupancy factor, and 10^{-6} is nano- to milli-conversion factor.

Keeping in view the atmospheric conditions of the area under study, population of the area on the average spends about 50% of the time outdoors; therefore, 0.5 was taken as the occupancy factor 'O' in this particular case. For the general public living in the area under study, the average annual effective dose was calculated to be 0.85 ± 0.29 (0.54–1.35) mSv y⁻¹ outdoors and 2.16 ± 0.74 (1.39–3.46) mSv y⁻¹ indoors. Total of the external indoor and outdoor dose is 3.01 ± 1.03 (1.94–4.81) mSv y⁻¹, which is about 6 times higher than the worldwide average of the annual effective dose of 0.48 mSv given in the report of UNSCEAR [20].

3.7.2. Radon dose

In order to investigate the annual mean effective dose H (mSv y⁻¹) due to radon and its progeny to the persons working in mines and warehouses, the concentration of radon was converted to effective dose by using the following relation [20]:

$$H = C \times F \times D \times T \times O \quad (4)$$

where C stands for radon concentration in Bq m⁻³, F for equilibrium equivalent concentration (EEC) factor, D for dose conversion factor (9×10^{-6} mSv h⁻¹ per Bq m⁻³), T for time (8760 h y⁻¹), and O for occupancy factor. The value of F as mentioned in the UNSCEAR report is 0.4 for the indoor environment and O was assumed to be 0.35 because the workers spend about 8–9 h per day in a fertilizer

warehouse. Annual effective dose due to radon inside and outside the phosphorite mines and inside the warehouses was calculated and is shown in Fig. 3 and is given in Table 8 respectively.

Radon effective dose in the warehouses varied between 0.19 and 0.58 with an average value of $0.36 \pm 0.14 \text{ mSv y}^{-1}$, which is less than that of worldwide environmental radon dose of 1.15 mSv y^{-1} [20]. The dose in the Peswal village, cave like mine, is almost double than that for other mines under consideration and is about two times more than that of the world average value.

4. Conclusions

Uranium makes chemical complexes with phosphate; therefore, PR contains natural radioactivity of uranium higher than its background level. The measured concentration of uranium in the phosphorite samples was $550 \pm 156 \text{ Bq kg}^{-1}$ which is higher than its maximum background value of 110 Bq kg^{-1} in soils of the various countries of the world. The samples of phosphorite formation and of hanging and foot walls could easily be distinguished due to vast contrast of radium activity concentration in the samples of different origin. Specific activity values of primordial radionuclides in PR samples were higher than, comparable to, or less than that for some countries of the world. Different geological origins of PR deposits are the main reason for the large spread in worldwide specific activities. Present study reveals that PR deposits of Abbottabad contain natural radioactivity considerably higher than background level. The phosphorite of Abbottabad is one of the sources of radioactive contamination in Pakistan.

Radiological hazard of the NORM in the phosphorite of Pakistan was assessed on the basis of models for radiation dose calculation. External dose rate values estimated for the studied sites are greater than the background level of activity of soil of the world. The concentration of radon measured in the phosphorite mines is greater than its permissible value. Radioactive pollution of phosphorite is a big health risk for the population concerned with PR and SSP fertilizer. Radiological hazard can be controlled through following protective measures: (a) training of the mineworkers regarding health physics and safety, (b) improving the living environment of the mines and dwellings, and (c) adopting the radiation protection guidelines to limit radiation exposure.

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References

- [1] B.U. Chang, S.M. Koh, Y.J. Kim, J.S. Seo, Y.Y. Yoon, J.W. Row, D.M. Lee, Nationwide survey on the natural radionuclides in industrial raw minerals in South Korea, *J. Environ. Radioact.* 99 (2008) 455–460.
- [2] F.T. daConceição, D.M. Bonotto, Radionuclides, heavy metals and fluorine incidence at Tapira phosphate rocks, Brazil, and their industrial (by) products, *Environ. Pollut.* 139 (2006) 232–243.
- [3] J. Bigu, M.I. Hussein, A.Z. Hussein, Radioactivity measurements in Egyptian phosphate mines and their significance in the occupational exposure of mine workers, *J. Environ. Radioact.* 47 (2000) 229–243.
- [4] J. Hofmann, R. Leicht, H.J. Wingender, J. Wörner, Natural radionuclide concentrations in materials processed in the chemical industry and the related radiological impact, in: *Nuclear Safety and the Environment*, European Commission, Report EUR 19264, Directorate-General Environment, 2000.
- [5] M.T. Hasan, Cambrian phosphorite deposits of the Hazara Division, North West Frontier Province, Pakistan, in: A.J.G. Notholt, R.P. Sheldon, D.F. Davidson (Eds.), *Phosphate Deposits of the World. Volume 2. Phosphate Rock Resources*, Cambridge Univ Press Cambridge, United Kingdom, 1989, pp. 449–454.
- [6] S.M. Jasinski, *Phosphate Rock, Minerals Year Book*, U.S. Geological Survey, 2003.
- [7] R.S. O'Brien, M.B. Cooper, Technologically enhanced naturally occurring radioactive material (NORM): pathway analysis and radiological impact, *Appl. Radiat. Isot.* 49 (1998) 227–239.
- [8] J.K. Otton, *Natural Radioactivity in the Environment*, U.S. Geological Survey, 1994.
- [9] H.A. Siddique, Phosphate rock deposits remain unexploited, *Economic and Business Review*, The Dawn Pakistan, October 16–22, 2006.
- [10] M. Asghar, M. Tufail, Sabiha-Javied, A. Abid, M. Waqas, Radiological implications of granite of Northern Pakistan, *J. Radiol. Prot.* 28 (2008) 387–399.
- [11] M. Tufail, Nasim-Akhtar, M. Waqas, Measurement of terrestrial radiation for assessment of gamma dose from cultivated and barren saline soils of Faisalabad in Pakistan, *Radiat. Meas.* 41 (2006) 443–451.
- [12] M. Tufail, Nasim-Akhtar, Sabiha-Javied, T. Hamid, Natural radioactivity hazards of building bricks fabricated from saline soil of two districts of Pakistan, *J. Radiol. Prot.* 27 (2007) 481–492.
- [13] Nasim-Akhtar, M. Tufail, Natural radioactivity intake into wheat grown on fertilized farms in two districts of Pakistan, *Radiat. Protect. Dosim.* 123 (2007) 103–112.
- [14] M. Tufail, N. Ahmad, H.A. Khan, M.S. Zafar, Gamma activity in the bricks used for the construction of dwellings in Rawalpindi and Islamabad areas of Pakistan, *Radiat. Protect. Dosim.* 37 (1991) 197–200.
- [15] M. Tufail, N. Ahmad, S.M. Mirza, N.M. Mirza, H.A. Khan, Natural radioactivity from the building materials used in Islamabad and Rawalpindi, Pakistan, *Sci. Total. Environ.* 121 (1992) 283–291.
- [16] M. Tufail, Radon and Gamma Activity Measurements for Determination of Radiation Doses, Assessment of Cancer Risks and Application to Geology/Geophysics, Department of Physics, University of the Punjab, Lahore, Pakistan, Dissertation, 1992.
- [17] M. Tufail, T. Rashid, A.B. Mahmood, N. Ahmad, Radiation doses in Pakistani houses, *Sci. Total. Environ.* 142 (1994) 171–177.
- [18] User Manual, Portable Radon Monior, "Alpha GUARD", Genitron Instruments GmbH, Germany, 1998.
- [19] R.W. Williams, K.D. Collerson, J.B. Gill, C. Deniel, High Th/U ratios in sub-continental lithospheric mantle: mass spectrometric measurement of Th isotopes in Gaussberg lamproites, *Earth Planet. Sci. Lett.* 111 (1992) 257–268.
- [20] UNSCEAR, Sources and Effects of Ionizing Radiation, United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York, 2000.
- [21] N.M. Mirza, B. Ali, S.M. Mirza, M. Tufail, N. Ahmad, A Shape and Mesh Adaptive Computational Methodology for Gamma Ray Dose From Volumetric Sources, vol. 38, Nuclear Technology Publishing, 1991, pp. 307–314, Centre for Nuclear Studies, PO Nilore, Rawalpindi, Pakistan.
- [22] CVCs (Colorado Vintage Companies Inc.), Radon decay product measurement, 2004, <http://www.coloradovintage.com/index.htm>, assessed on 9th June, 2009.
- [23] EPA (Environmental protection Agency), Assessment of Risks From Radon in Homes, Air and Radiation EPA 402-R-03-003, 2003.
- [24] M. Tufail, Nasim-Akhtar, M. Waqas, Radioactive rock phosphate: the feed stock of phosphate fertilizers used in Pakistan, *Health Phys.* 90 (2006) 361–370.
- [25] M. Olszewska-Wasiolek, Estimates of the occupational radiological hazards in phosphate fertilizers industry in Poland, *Radiat. Protect. Dosim.* 58 (1995) 269–276.
- [26] L.C. Scholten, C.W.M. Timmermans, Natural radioactivity in phosphate fertilizers, *Nutr. Cycl. Agroecosyst.* 43 (1995) 103–107.
- [27] A.E.M. Khater, H.M. Higgy, M. Pimpl, Radiological impacts of natural radioactivity in Abu-Tartor phosphate deposits, Egypt, *J. Environ. Radioact.* 55 (2001) 255–267.
- [28] E.M. Hussein, Radioactivity of phosphate ore, superphosphate and phosphogypsum in Abu-Zaabal phosphate plant, Egypt, *Health Phys.* 67 (1994) 280–282.
- [29] R. Mustonen, Radioactivity of fertilizers in Finland, *Sci. Total. Environ.* 45 (1985) 127–134.
- [30] R.J. Guimond, Radium in Fertilizers: Environmental Behaviour of Radium, International Atomic Energy Agency, IAEA Technical Report 310, Vienna, 1990, pp. 113–128.
- [31] M. Azouazi, Y. Ouahidi, S. Fakhri, Y. Andres, J. Ch. Abbe, M. Benmansour, Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco, *J. Environ. Radioact.* 54 (2001) 231–242.
- [32] P.O. Ogunleye, M.C. Mayaki, I.Y. Amapu, Radioactivity and heavy metal composition of Nigerian phosphate rocks: possible environmental implications, *J. Environ. Radioact.* 62 (2002) 39–48.
- [33] A. Aksoy, M. Ahmed, W.S.A. Matter, Z.R. El-Naggar, Gamma-ray spectroscopic and PIXE analysis of selected samples from the phosphorite deposits of North-western Saudi Arabia, *J. Radioanal. Nucl. Chem.* 253 (2002) 517–521.
- [34] A.K. Sam, E. Holm, The natural radioactivity in phosphate deposits from Sudan, *Sci. Total. Environ.* 162 (1995) 173–178.
- [35] M.M. Makweba, E. Holm, The natural radioactivity of the rock phosphate, phosphatic products and their environmental implications, *Sci. Total. Environ.* 133 (1993) 99–110.
- [36] F.P. Banzi, L.D. Kifanga, F.M. Bundala, Natural radioactivity and radiation exposure at the Minjingu phosphate mine in Tanzania, *J. Radiol. Prot.* 20 (2000) 41–51.
- [37] T. Akyuz, S. Akyuz, A. Varinlioglu, A. Kose, Radioactivity of phosphate ores from Karatas-Mazidag phosphate deposit of Turkey, *J. Radioanal. Nucl. Chem.* 243 (2000) 715–718.

- [38] C.E. Rossler, Z.A. Smith, W.E. Bolch, R.J. Prince, Uranium and radium-226 in Florida phosphate materials, *Health Phys.* 37 (1979) 269–277.
- [39] M.N. Alam, M.I. Chowdhury, M. Kamal, S. Ggose, H. Banu, D. Chakraborty, Radioactivity in chemical fertilizer used in Bangladesh, *Appl. Radiat. Isot.* 48 (1997) 1165–1168.
- [40] C.H. Saueia, B.P. Mazzilli, D.I.T. Fávoro, Natural radioactivity in phosphate Rock, phosphogypsum and phosphate fertilizers in Brazil, *J. Radioanal. Nucl. Chem.* 264 (2005) 445–448.
- [41] C.H.R. Saueia, B.P. Mazzilli, Distribution of natural radionuclides in the production and use of phosphate fertilizers in Brazil, *J. Environ. Radioact.* 89 (2006) 229–239.
- [42] F.T. Conceição, D.M. Bonotto, Radiological incidence at Tapira and Catalão phosphate rocks, their (by) products, phosphate fertilizers and amendments, in: *Short Papers–IV South American Symposium on Isotope Geology*, 2000.
- [43] N.M. Mourad, T. Sharshar, T. Elnimr, M.A. Mousa, Radioactivity and fluoride contamination derived from a phosphate fertilizer plant in Egypt, *Appl. Radiat. Isot.* 67 (2009) 1259–1268.
- [44] H. Pfister, G. Philipp, H. Pauly, Population dose from natural radionuclides in phosphate fertilizers, *Radiat. Environ. Biophys.* 13 (1976) 247–261.
- [45] K. Brigden, R. Stringer, D. Santillo, Heavy Metal and Radionuclide Contamination of Fertilizer Products and Phosphogypsum Waste Produced by the Lebanese Chemical Company. Lebanon, Greenpeace Research Laboratories, Technical Note 13, 2002.
- [46] R.J. Guimond, J.M. Hardin, Radioactivity released from phosphate containing fertilizers and from gypsum, *Radiat. Phys. Chem.* 34 (1989) 309–315.