Measurement of natural radioactivity in soil from Peshawar basin of Pakistan

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Abstract Natural radioactivity in the environment may change with time due to human activities, chemical and biological changes. From the view of radiation risk to population, the knowledge of natural radioactivity levels and the measurement of collective radiation dose received by the population is very vital. Radiological constraints on soil of thickly populated Peshawar basin in northern Pakistan were assessed through radiometric assay. Soil samples collected from different locations of four districts of this basin were analysed using an HPGe gamma spectrometer. Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in these samples was 648 ± 121 (421–996), 45 ± 7 (32–60) and 59 ± 7 (46–72) Bq kg^{-1}, respectively that followed lognormal distribution. The average concentrations of primordial radionuclides were found to be higher than that reported for the worldwide soil. Radium equivalent activity and gamma index derived from these activity concentrations were lesser than their respective limits. The average absorbed dose rate and the annual effective dose for both indoor and outdoor cases were found to be higher than the values given in the UNSCEAR 2000 report. The results of the present study were compared with those for other locations of Pakistan along with that for the world. The radiological impact of the measured data was evaluated using hazard assessment models. A thoughtful discussion of the above mentioned evaluation is also given.

Introduction

Soil is the upper layer of the earth's crust and is composed of mineral particles, organic matter, water, air and organisms [1]. It is formed as a result of weathering of rocks in the earth's crust and deposition of eroded materials into depressions. Primordial radionuclides present in these rocks are also passed through the processes of erosion and deposition and have become an integral part of the soil. The long-lived primordial radionuclides found in soil are ^{40}K, ^{238}U, ^{235}U and ^{232}Th along with the decay products of uranium and thorium series [2]. Half-lives of these nuclides are of the order of the age of the earth. Therefore, such nuclides are still present in the soil.

Human beings are exposed internally to radon and externally to gamma rays emitted from the naturally occurring radioactive material (NORM) present in soil. The emitted gamma radiations from the NORM in the earth's crust are called terrestrial background radiations [2]. The specific levels of terrestrial radiation and the associated radiation exposure are related to the geological composition of each lithaology of the area and the contents of the NORM in the rocks from which the soil originated [3, 4]. The dose rate due to these radionuclides varies from place

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to place depending upon their concentration level in the soil. The main external source of radiation from natural sources to the human body comes from terrestrial gamma radionuclides [5]. For the measurement of natural radioactivity in different materials around the world, a number of different techniques have been employed [6–14].

The study area lies in the region, which is geologically known as Peshawar basin (Fig. 1). The area and population of each district of the understudy area are given in Table 1 in accordance with the census of Pakistan carried out in 1998. The tectonic setting of the basin is transitional between a sedimentary fold and thrust belt to the south and metamorphic terrain to the north. The inlithified sediments

of the Peshawar basin are predominantly lacustrine silts with fluvial sand and gravel. The basin came into existence in Plio-Pleistocene time with termination of sedimentation about 600,000 years ago when more than 300 m of sediments were deposited in response to pending of drainage by the rising Attock Cherat Range [15]. Exposures of the Paleozoic and older strata are limited to small outcrops within the basin. The radioactive content in soil of the area understudy depends on the geology of the area and the surrounding mountains where the material was eroded and transported by rainwater into the basin.

The erosion and deposition of rocks in the Peshawar basin of Pakistan have generated a high quality soil suitable for the

Fig. 1 The map of Pakistan showing the Peshawar basin and location of the districts in the study area
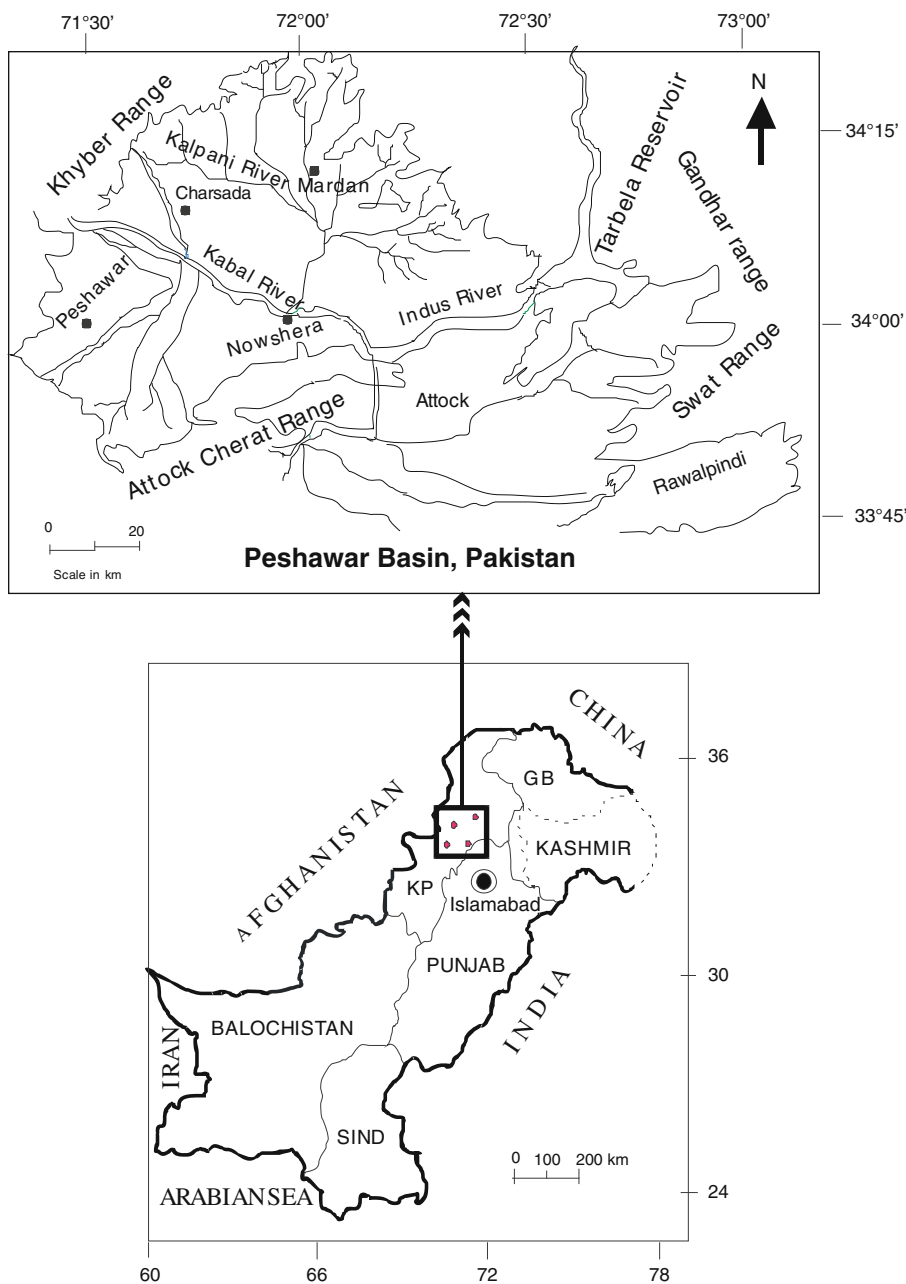
Table 1 The location, area and population of four districts in the Peshawar basin of Pakistan

Study area	Names of Tehsils	Latitude (N)	Longitude (E)	Area (km^2)	Population ($\times 10^6$)
Charsada	Charsada, Tangi	34°09′(34°12′–34°36′)	71°44′(71°30′–71°54′)	996	1.02
Nowshera	Nowshera	34°01′(33°36′–34°18′)	71°58′(71°36′–72°18′)	1,748	0.87
Mardan	Mardan, Takht Bhai	34°12′(34°05′–34°32′)	72°01′(71°48′–72°25′)	1,632	1.46
Peshawar	Peshawar	34°00′(33°42′–34°12′)	71°30′(71°26′–71°48′)	1,257	2.02

cultivation of crops and construction of dwellings. Soil-based dwellings include houses made of baked and unbaked clay bricks, adobes made of mud rolls, and caves dug into the elevated land or hills of soil. The kiln-baked bricks made of this soil are widely distributed in various parts of the country. The population working in the agricultural fields is exposed externally to terrestrial gamma rays whereas the habitants of these soil-based dwellings are exposed internally and externally to radon and gamma radiation. The extensive use of soil of the area led us to the measurement of natural radioactivity levels and evaluation of corresponding radiological health hazards associated with background radioactivity of soil and the building bricks. The hazards are normally estimated by taking into account the collective effect of activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th by a single quantity called hazard index. The most commonly applied radiological hazard indices, defined by various radiation protection agencies as well as UNSCEAR-2000, used in this study includes; radium equivalent activity, gamma index, annual effective doses for both indoor/outdoor cases, etc.

Present study was undertaken within the framework of our countrywide radiological environmental monitoring programme with the collaboration of National Universities and other research institutes of the country. The main objective of this programme is to assess the type and amount of natural and man-made radioactivity levels in drinks, food items, building materials and other samples from environmental media. Radiological environmental monitoring survey for some specific areas of Pakistan has already been accomplished and the results are published elsewhere [16–21]. In this study radiological hazards associated with soil samples, in terms of radium equivalent activity (Ra$_{eq}$), gamma index (I$_\gamma$), indoor external dose rate ($\dot{D}_{in}$), outdoor external dose rate ($\dot{D}_{out}$), indoor annual effective dose (E_{in}) and outdoor annual effective dose (E_{out}) were evaluated. The results were also compared with similar work reported for other countries of the world.

Area of study

Peshawar basin lies in Khyber Pakhtunkhawa (KP) province of Pakistan. The basin, covering an area of 5,500 km^2, is situated at the southern foothills of Himalayas between longitudes 71°15′–72°45′E and latitudes 33°45′–34°30′N in the KP province of Pakistan (Fig. 1). The Basin is surrounded by Khyber, Swat and Attock-Cherat mountain ranges in the north-west, north-east and south respectively. It is major tectonic sag [22]. Proterozoic and Paleozoic rocks lie north of this basin, and a few tens of kilometers north of the eastern part of the study area are granitic stock and the Kohistan island arc complex [22, 23]. The Peshawar basin comprises a sequence of Cambrian to Jurassic rocks resting on a Precambrian basement [23]. The Basin has a thick Plio-Pleistocene to Holocene fill of alluvial sediments that began accumulating at least 2.8 m.y. ago [21, 24]. Sediments accumulated at an average rate of 15 cm ky^{-1} [24]. The basin began receiving sediments in Pliocene time. The basin is coeval with the syntaxis and lacustrine sedimentation, although its overall history is that of surface uplift [25]. Burbank and Khan Tahirkheli emphasise that this lacustrine sedimentation contrasts with the fluvial sedimentation that is predominant in adjacent areas [24].

The stratigraphic sequence exposed in the Peshawar basin can well be observed in Nowshera, Ghandhar and Attock-Cherat range. These are generally Pre-Cambrian to Devonian metasediments. Three structural blocks, separated by thrust faults, are present within the Attock-Cherat range [22]. The northern block is composed of the Pre-Cambrian Manki, Shahkot, Utch, Khuttak and Shekhai formations, the central block is largely made up of Pre-Cambrian Dakhner formation, whereas the southern block consists of a north dipping homclinal sequence i.e. Darwaza, Hisartang and Inzi formations [22].

Soil of the Peshawar basin is the ground underfoot, a relatively thin layer of the earth crust that has been modified by the natural actions of agents such as weather, wind, water and organism. Climate, parent material topography, time, plants, and organic activities play significant role in the formation of the soils. The soil of the area is polluted by applications of agrochemicals, release of sludge, and waste water from municipalities and industries. The west-east flowing river Kabul and its tributaries irrigate the basin and join the river Indus at eastern exit.

Materials and methods

Sample management

A total of 71 samples of soil were collected randomly from the districts of Charsada, Mardan, Nowshera and Peshawar in the Peshawar basin of Pakistan. The samples were collected randomly covering most of the area of the four districts. Each sample was a representative of five soil specimens. One specimen was obtained from the central site while others four were collected around the central point having a radius of 50–100 km from the depth of 10–30 cm [26]. The specimens were crushed into small pieces, mixed uniformly. Approximately 1 kg of this mixture was taken as one sample in a polythene lined cloth made bag. After proper numbering and cataloguing the samples were initially dried in the sun and then heated in a microprocessor-controlled oven at 110 °C for 24 h to remove moisture from the samples. The samples were then pulverized to powder, passed through a sieve of 100 μm mesh size, and packed in the airtight polyvinyl chloride containers having dimensions of 75 mm diameter and 37 mm height [27]. Reference materials Soil–375 and Soil–6 obtained from the Analytical Quality Control Services (AQCS) of International Atomic Energy Agency (IAEA) were also put in the airtight containers of same material and dimensions. The densities of the samples and reference materials were kept identical in packing containers. Before measuring activity concentrations, it is necessary to achieve secular equilibrium between ^{226}Ra and ^{222}Rn and its short-lived progenies in the samples [28]. The equilibrium time (t) for the storage was calculated using the following equation [29, 30]:

$$t = \frac{\ln(\lambda_2/\lambda_1)}{\lambda_2 - \lambda_1} \tag{1}$$

where λ_1 and λ_2 are decay constants of ^{226}Ra and ^{222}Rn respectively which gives the value of 't' equal to 67 days. To ensure the secular equilibrium between them, soil samples along with the reference materials were stored for about 2 months.

Radiometric assay

Activity concentration of the soil samples was determined using an HPGe detector with vertical cryostat manufactured by ORTECH. The detector was n-type coaxial configuration having crystal diameter of 55.7 mm and length 72.1 mm. The cryostat was dipped vertically into a liquid nitrogen container of size 30 L. The detector was kept in a 10 cm lead shielded cavity of volume 30 cm × 30 cm × 30 cm with successive linings of copper, aluminium and perspex of about 2 mm thickness of each. The output

of the detector was fed to a personnel computer (PC) based multichannel analyzer containing a hardware card with inbuilt amplifier and an analogue to digital converter. For data acquisition and analysis, the software of APTEC was installed in the PC. After energy calibration with point sources, the full width half maximum of the detection system was measured to be 1.85 at 1332.5 keV of ^{60}Co point source kept at a distance of 25 in front of the face of the HPGe detector. From the inbuilt library of radionuclides, the nuclides ^{40}K, the progeny of ^{238}U and ^{232}Th were selected for energy and efficiency calibration purposes. For efficiency calibration of the system, spectra of Soil–375 and backgrounds were collected for 7.2×10^4 s. Area under every energy peak was determined using the automatic search facility of the software. After subtracting the background from the soil spectrum, the areas under the peaks and the present activities as per certificate of the reference material was used to calculate the peak efficiency [31]. The following polynomial was fitted to the plot of efficiency η versus energy E.

$$\log \eta = 2.95 - 2.51 \,[\log(E)] + 0.23 \,[\log(E)]^2 \tag{2}$$

The polynomial and efficiency curve were stored in the PC. A graph of percentage efficiency versus $\log(E)$ is shown in Fig. 2. Energy spectrum of every sample was also collected for 7.2×10^4 s. Background was subtracted and activity concentration (A) of ^{40}K, ^{226}Ra and ^{232}Th in Bq kg^{-1} was determined using relation:

$$A = \frac{R}{y \times \eta \times m} \tag{3}$$

where 'R' is the net count rate (i.e. the gross count rate minus the background count rate), 'y' is the gamma yield, 'η' is the efficiency of the detectors for corresponding peak which was determined using the efficiency–polynomial already stored in the PC and 'm' is the mass of sample in kg. The quality control was checked with Soil–6, the
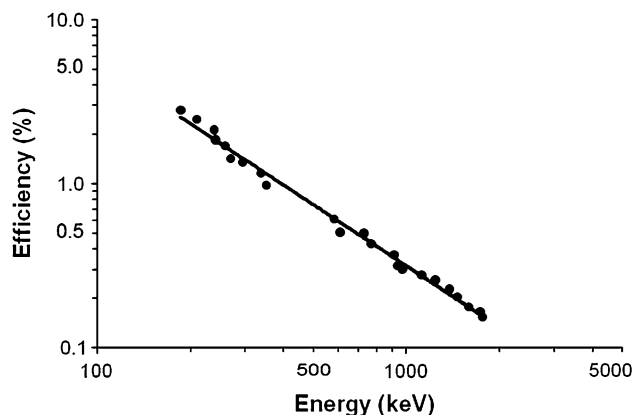

Fig. 2 Detector peak efficiency versus gamma ray energy

measured activity of which was within ± 10 % of the quoted value.

Gamma ray energies 295.21 (19.20 %), 351.92 (35.10 %), 609.32 (44.60 %), 1120.28 (14.70 %) and 1764.52 (15.10 %) keV were used for the calculation of ^{226}Ra concentration, the energies 238.63 (43.50 %), 338.42 (11.26 %), 583.19 (30.58 %), 911.16 (26.60 %), 968.97 (16.23 %) and 2641.60 (35.80 %) keV were considered for the determination of ^{232}Th concentration; and the energy 1460.80 (10.67 %) keV was taken into account for the measurement of ^{40}K concentration. The value within parenthesis is the percent emission yield or abundance of gamma of specified energy.

Population weighted mean activity concentrations ($\overline{A}_{i-pop}$) was also calculated for ^{40}K, ^{226}Ra and ^{232}Th using the formula:

$$\overline{A}_{i-pop} = \frac{\sum\limits_{j=1}^{n} \overline{A}_i \times P_j}{\sum\limits_{j=1}^{n} P_j} \tag{4}$$

where, i and j are the ith radionuclide and jth district respectively; $\overline{A}_i$ is the arithmetic mean activity concentration of ith radionuclide in Bq kg^{-1} given in Table 2; P_j is the population of the jth district and n is the number of districts considered in the area of interest. The calculated values of $\overline{A}_{i-pop}$ are given in Table 5. The population weighted mean activity concentration values of ^{40}K, ^{226}Ra and ^{232}Th for the Punjab province were 670, 33 and 49 Bq kg^{-1}, respectively, while for the KP were 628, 43 and 59 Bq kg^{-1} and the respective values for the soil of the Peshawar basin were 624, 44 and 58 Bq kg^{-1}.

Radiological hazard

The radiological hazard associated with the exposure to radiation was determined to evaluate the radioactivity level in the region against certain radiation protection standards. The hazard of radiation was estimated by taking into account the collective effect of activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th by a single quantity called hazard index. The most commonly applied radiological hazard indices defined by various radiation protection agencies and by some individuals used in this study are described as follows:

Radium equivalent activity

The exposure due to measured radiation in term of radium equivalent activity defined by Beretka and Methew was calculated using relation [32]:

$$Ra_{eq} = A_{Ra} + \frac{10}{7} A_{Th} + \frac{10}{130} A_K \tag{5}$$

where, A_{Ra}, A_{Th} and A_K denote the measured activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1} respectively. In defining the Ra_{eq}, it was estimated that 10 Bq kg^{-1} of ^{226}Ra, 7 Bq kg^{-1} of ^{232}Th, and 130 Bq kg^{-1} of ^{40}K deliver equal radiation dose. The recommended maximum activity level of Ra_{eq} in materials corresponding to annual dose of 1.5 mGy is 370 Bq kg^{-1}.[34] The sub-multiple of Ra_{eq} defined as the external hazard index, H_{ex} was calculated using the relation [33]:

$$H_{ex} = \frac{Ra_{eq}}{370} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{6}$$

To keep the annual dose <1.5 mGy y^{-1}, the condition $H_{ex} < 1$, has to be satisfied.

Gamma index

The European Commission has proposed an index called the gamma index (I_γ) defined by the following relation [34]:

$$I_\gamma = \frac{A_{Ra}}{300} + \frac{A_{Th}}{200} + \frac{A_K}{3000} \tag{7}$$

Materials having $I_\gamma \leq 2$ will make an increase of 0.3 mSv in the annual effective dose whereas $2 < I_\gamma \leq 6$

Table 2 Activity concentrations of the primordial radionuclides in the soil samples collected from four districts in Peshawar basin of Pakistan	District	Samples	Statistical values	Activity concentration (Bq kg^{-1})		
				^{40}K	^{226}Ra	^{232}Th
	Charsada	20	Range	648–996	40–60	56–72
			AM ± SD	784 ± 88	50 ± 5	64 ± 4
	Mardan	20	Range	421–761	34–56	49–69
			AM ± SD	576 ± 78	43 ± 6	58 ± 7
	Nowshera	15	Range	503–833	32–55	46–66
			AM ± SD	652 ± 104	46 ± 7	59 ± 7
	Peshawar	16	Range	495–627	33–51	46–67
			AM ± SD	565 ± 45	41 ± 5	55 ± 6

correspond to an increase of 1 mSv y^{-1} [34, 35]. According to the recommendations of the European Commission, the materials that do not increase the annual effective dose of a member of public by 0.3 mSv at the most should be exempted from all restrictions concerning to radioactivity hazard [36]. On the other hand, the doses higher than 1 mSv y^{-1} are allowed only for exceptional cases where materials are used locally.

Outdoor external dose

Assuming that ^{40}K, ^{226}Ra and ^{232}Th were distributed uniformly in the soil of the study area, external dose rate at 1 m above the ground surface was calculated from the measured activity concentration of ^{40}K, ^{226}Ra and ^{232}Th using the following activity to dose rate conversion formula [5]:

$$\dot{D}_{out} = 0.0417A_K + 0.462A_{Ra} + 0.604A_{Th} \qquad (8)$$

where $\dot{D}_{out}$ is the absorbed dose rate in nGy h^{-1}. The coefficients 0.0417, 0.462 and 0.604 are the activity concentration to dose rate conversion factors of A_K, A_{Ra} and A_{Th} respectively in nGy h^{-1} per Bq kg^{-1}.

Outdoor annual effective dose was estimated on the basis of calculated absorbed dose rate by taking into account (a) the outdoor occupancy factor $O_{out} = 0.2$ and (b) the conversion coefficient from absorbed dose rate in air to effective dose $C = 0.7$ Sv Gy^{-1} for the adults. Following equation was used for the estimation of annual effective dose [5]:

$$E_{out} = \dot{D}_{out} \times O_{out} \times C \times 8760 \times 10^{-6} \qquad (9)$$

where E_{out} is the outdoor annual effective dose in mSv y^{-1}.

Indoor external dose

Soil is very popular building material in Pakistan and is used for the construction of dwellings in different forms. Houses in cities and countryside are constructed from the baked and unbaked clay bricks respectively. Mud, a kind of soil, is used to make houses by the low-income people.

Based on the assumption that the primordial radionuclides have uniform distribution in clay bricks, the indoor external dose rate (nGy h^{-1}) was calculated for a model room having dimension $4 \times 5 \times 2.8$ m^3 and wall thickness of 20 cm by the following relation [36]:

$$\dot{D}_{in} = 0.1A_K + 1.21A_{Ra} + 1.29A_{Th} \qquad (10)$$

where 0.1, 1.21 and 1.29 are the activity to indoor dose rate conversion factors in nGy h^{-1} per Bq kg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th respectively. The indoor external dose rate in air from the bricks made up of the soil from the Peshawar basin was converted to the effective annual dose rate [5]:

$$E_{in} = \dot{D}_{in} \times O_{in} \times C \times 8760 \times 10^{-6} \qquad (11)$$

where E_{in} is the effective dose rate in mSv y^{-1}, $\dot{D}_{in}$ is the indoor external dose rate in air (nGy h^{-1}), C is the dose rate in air to effective dose conversion factor (0.7 Sv Gy^{-1}) and O_{in} is the indoor occupancy factor taken as 0.8 [5].

Results

The activity concentration values of ^{40}K, ^{226}Ra and ^{232}Th measured in the soil samples of the understudy is given in Table 2. The arithmetic mean, standard deviation in mean, and range (minimum–maximum) of the measured concentrations of the radionuclides in soil of every district is presented in this table. The associated statistical error, at 68 % confidence level, is 8–16 % for ^{40}K, 10–14 % for ^{226}Ra, and 6–12 % for ^{232}Th.

The dependence of these radionuclides upon each other in terms of linearly fitted correlation coefficients and activity concentration ratios analyzed for the four districts are presented in Table 3. The ratios are given in the form of the mean and range (minimum–maximum) values. The correlation coefficients and activity ratios of the radionuclides in the soil of Peshawar basin are also presented in Table 3. The correlation of the radionuclides in Peshawar basin given is Table 3 is better than that in every district.

Table 3 The correlation coefficients and ratios of activity concentrations of radionuclides in soil from four districts of Peshawar basin in Khyber Pakhtunkhwa, Pakistan

Location	Correlation coefficient			Ratio		
	^{40}K–^{226}Ra	^{40}K–^{232}Th	^{226}Ra–^{232}Th	^{232}Th/^{226}Ra	^{40}K/^{226}Ra	^{40}K/^{232}Th
Charsada	0.69	0.71	0.58	1.3 (1.1–1.5)	15.9 (13.2–18.5)	12.2 (10.3–13.8)
Mardan	0.79	0.50	0.78	1.4 (1.1–1.6)	13.3 (10.8–15.9)	9.9 (7.8–12.2)
Nowshera	0.65	0.61	0.65	1.3 (1.0–1.6)	14.4 (9.8–17.2)	11.1 (7.8–13.3)
Peshawar	0.21	0.12	0.47	1.4 (1.0–1.6)	13.9 (9.8–17.2)	10.3 (7.8–12.9)
Peshawar basin	0.73	0.63	0.72	1.3 (1.0–1.6)	14.4 (9.8–18.5)	10.9 (7.8–13.8)

The overall statistical behavior of the measured activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the soil of Peshawar basin (four districts) is given in Table 4 that include range, arithmetic mean with standard deviation, geometric mean, geometric standard deviation, median, mode, skewness, kurtosis co-efficient and the type of frequency distribution for these radionuclides in the soil samples. The overall activity concentration of ^{40}K was in the range of 421–996 Bq kg^{-1} with an average value of 648 ± 121 Bq kg^{-1}. The activity concentration of ^{226}Ra in the Peshawar basin (four districts) varied from 32–60 Bq kg^{-1} with an average value of 45 ± 7 Bq kg^{-1} and that of ^{232}Th varied from 46–72 Bq kg^{-1} with an average value of 59 ± 7 Bq kg^{-1}. The ± error quoted is the standard deviation from the arithmetic mean.

To see the statistical spread of ^{40}K, ^{226}Ra and ^{232}Th in the soil of Peshawar basin, the measured activity concentrations in all the samples of soil from the understudy four districts are presented in Fig. 3 by the frequency distribution plots. The radionuclides are not symmetrically distributed rather skewed towards right.

The linearly fitted correlation coefficients of three major natural nuclides were also computed for the soil of Peshawar basin and found equal to 0.73, 0.63 and 0.72 respectively for ^{40}K–^{226}Ra, ^{40}K–^{232}Th and ^{226}Ra–^{232}Th combinations. The correlation between ^{226}Ra and ^{232}Th in the soil of Peshawar basin is presented in Fig. 4.

Discussion

Among the average values of the activity concentrations given in Table 2, the concentration of ^{40}K, ^{226}Ra and ^{232}Th are the lowest in the soil of Peshawar and the highest in the soil of Charsada district. This may be due to different modes of irrigation, fertilization and pollution of the soil of the districts in Peshawar basin.

Table 3 depicts a good correlation of ^{40}K–^{232}Ra and ^{40}K–^{226}Ra and ^{226}Ra–^{232}Th in the soil of Charsada, Mardan and Noshera districts, but a poor correlation of ^{40}K–^{232}Th and ^{40}K–^{226}Ra and a fair correlation of ^{226}Ra–^{232}Th in the soil of Peshawar district. The poor correlation of potassium with radium and thorium may be the instability of the potassium minerals in the soil of Peshawar district. The stability is strongly temperature and pressure dependent and thus subject to alteration during diagenetic processes. Potassium is a major element in many rock forming minerals and is present in almost all crustal rocks and is enriched in claystones. During weathering of crystalline rocks, potassium is readily dissolved therefore may have been removed from the soil of understudy soil. A fair correlation between ^{226}Ra and ^{232}Th is expected for an area of homogeneous soil. The ^{238}U and ^{232}Th series occur commonly together in nature and this weak correlation may be due to soil processes that affect differently the mobility of the two radionuclides.

The concentration ratios given in Table 3 may provide an indication whether relative depletion or enrichment of radionuclides had occurred. Activity concentration ratio $^{232}Th/^{226}Ra$ was observed to be greater than unity for all the samples indicating that the activity concentration of Th was greater than that of Ra in the area. This was in accordance with the worldwide trend of ^{232}Th activity in upper crust of the earth probably due to longer half life of ^{232}Th than that of ^{238}U [37]. The theoretically expected Th/U ratio for normal continental crust is about 3.0, while the corresponding value obtained for this ratio is (1.0–1.6), which indicate that significant fractionation during weathering or involvement in metasomatic activity of the radio-elements had occurred. The potassium/uranium (K/U) ratio for the analyzed soils is 10–19, which is lower than the value for normal continental, crust estimated as $(1.0–1.3) \times 10^4$. The ratio between potassium and thorium concentrations (K/Th) 8–14 is also lower than the normal continental crustal value.

Table 4 Statistical data for activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th and (Bq kg^{-1}) in surface soil samples from the Peshawar basin of Pakistan

Statistical parameter	Activity concentrations (Bq kg^{-1})			
	^{40}K	^{226}Ra	^{232}Th	Ra$_{eq}$
Range	421–996	32–60	46–72	139–237
Arithmetic mean (AM)	648	45	59	180
Standard deviation (SD)	121	7	7	23
Geometric mean (GM)	637	44	58	178
Geometric standard deviation (GSD)	1.2	1.2	1.1	1.1
Median	619	45	61	176
Mode	545	39	57	159
Skewness	2.9	3.1	2.8	1.8
Kurtosis	3.9	4.2	3.5	2.7
Frequency distribution	Lognormal	Lognormal	Lognormal	Lognormal
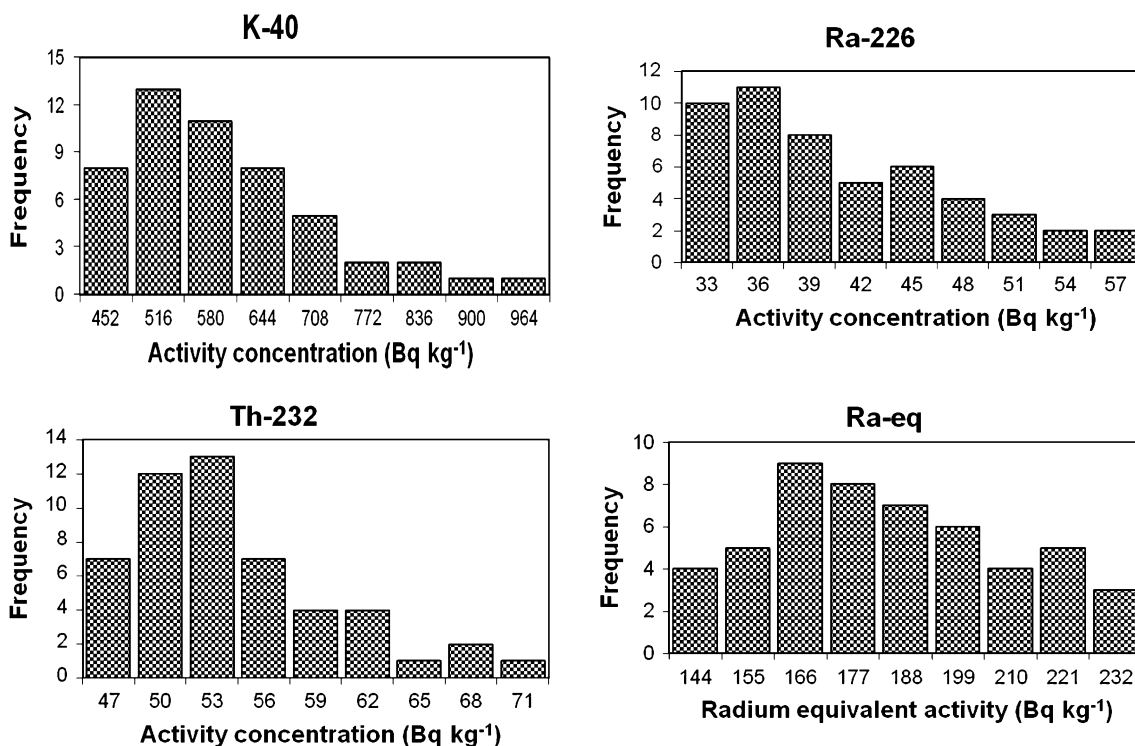
Fig. 3 Frequency distribution plots for activity concentrations of [40]K, [226]Ra, [232]Th and Ra$_{eq}$ in soil samples from the understudy area
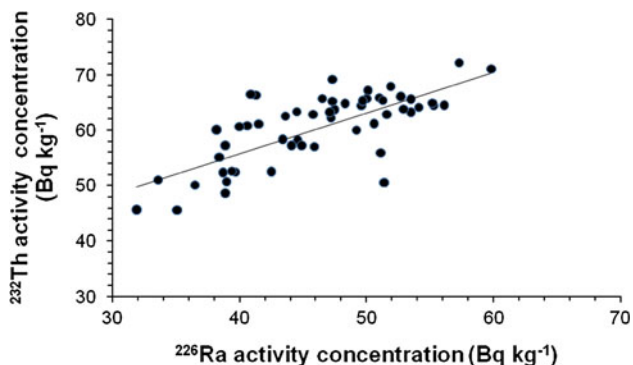
Fig. 4 The linear correlation of [226]Ra–[232]Th activity concentrations in soil samples of Peshawar basin

The arithmetic and geometric mean concentrations given in Table 4 are observed to be the highest for [40]K, followed by [232]Th and the lowest mean activity was observed for [226]Ra. This is in accordance with the concentrations of uranium, thorium and potassium in the earth's crust. Among the mean values, the minimum of activity concentration of the three radionuclides belonged to district Peshawar and the maximum was in the samples from Charsada. The values of skewness and kurtosis coefficients for all the three radionuclides are away from the null value, indicating the absence of normal distribution. The positive values of kurtosis coefficient given for

these radionuclides also indicate that the distributions are higher and narrower than normal [38].

The frequency plots of Fig. 3 show that the radionuclides do not follow normal distribution. The nonexistence of normal distribution was verified by the calculations for normal distribution based on arithmetic mean and the frequency values. The existence of lognormal distribution was confirmed by the calculation for normal distribution based on geometric mean and logarithm of the frequency values. Moreover, if the distribution is lognormal, then the geometrical mean should be equal to the median value. It can be observed from Table 4, the values of both the parameters are near to each other, and therefore the distribution is close to the lognormal distribution. The distribution is skewed to the right, containing points with relatively high magnitude, several times the mean. The mean tends to overestimate exposure of the public to radioactivity. In this case, some individuals are exposed to high concentrations, but the average person is exposed to lower concentrations than the mean suggests and a mode or a median is more meaningful in this situation.

The association between the radionuclides in the soil of Peshawar basin presented in Table 3 and shown in Fig. 4 portrays that the individual results for any radionuclide pair are good predictor of the concentration of the other. They belong to same source and soil not contaminated of any other source.

To compare the activity concentration of the radionuclides measured in the soil of the understudy districts with that of the other districts of Pakistan, data has been compiled from literature and given in Table 5. Among the districts in comparison, Multan has the maximum activity concentration of [40]K, while Charsada district has the maximum value of [226]Ra and [232]Th. Rawalpindi district has the minimum values of all the three nuclides.

The weighted average activity concentrations of [40]K, [226]Ra and [232]Th for the provinces of the Punjab and KP was calculated by averaging the activity concentration data of the districts and is given at the end of each provincial districts in Table 5. Activity concentration level of [40]K in the Punjab was comparable to that in the KP province. Similarly activity level of [226]Ra was 22 % higher for the KP than their corresponding values in the Punjab while the value of [232]Th was 29 % higher for the KP than Punjab. The higher values of [226]Ra and [232]Th in soil the Peshawar basin may be attributed to the sedimentation from the surrounding mountain ranges. The average specific activities of [40]K, [226]Ra and [232]Th in the soil of Peshawar basin were 62, 29 and 97 % respectively higher than their corresponding worldwide median values of 400, 35 and 30 Bq kg^{-1}. The population weighted specific activities of these nuclides were 48, 38 and 30 % higher than their respective worldwide values 420, 32 and 45 Bq kg^{-1} given in the report of UNSCEAR.

As may be seen from the data of two provinces given in Table 5, the overall average activity concentration concentrations of [40]K, [226]Ra and [232]Th was determined to be 651, 39 and 55 Bq kg^{-1} respectively. These values can be considered as the representative values for Pakistan. We have compiled data from literature on activity concentration in soil for some countries from Asia and listed in Table 6. From this data the median/mean and range (given in parenthesis) of activity concentrations of [40]K, [226]Ra and [232]Th were determined to be 486 (129–994), 48 (16–137) and 53 (17–109) Bq kg^{-1}. The comparison shows that the average concentration of [40]K in soil of the Peshawar basin is higher than that of Asia, while the concentrations of [226]Ra and [232]Th are comparable within statistical uncertainty. Activity concentrations of [40]K, [226]Ra and [232]Th in the soil of Peshawar basin, Pakistan and Asian countries are higher than the corresponding values in the worldwide soil [5].

Table 5 Comparison of the average values of activity concentrations of primordial radionuclides in soil samples from different districts of the Punjab province with present work

| Province | Population | Activity concentration (Bq kg^{-1}) | | |
District	×10^6	[40]K	[226]Ra	[232]Th
Punjab				
Bhawalpur [40]	2.43	647	33	54
Sialkot [41]	2.72	698	42	49
Faisalabad [30]	5.43	602	30	56
Gujranwala [41]	3.40	658	33	42
Islamabad [42]	0.81	690	38	59
Lahore [43]	6.32	570	18	28
Mianwali [44]	1.06	481	34	55
Multan [45]	3.12	945	42	52
Rawalpindi [41]	3.36	399	22	32
Sargodha [42]	2.67	635	43	45
Khan [41]	0.85	657	39	61
Weighted average		654	34	49
Population-weighted average		670	33	49
Khyber Pakhtunkhwa/Peshawar basin				
Charsada (present work)	1.02	784	50	64
Nowshera (present work)	0.87	652	46	59
Mardan (present work)	1.46	576	43	58
Peshawar (present work)	2.02	565	41	55
Weighted average		647/624	44/45	60/59
Population-weighted average		628/624	43/44	59/58
Overall (Punjab + Khyber Pakhtunkhwa)				
Weighted average		651	39	55
Population-weighted average		663	34	50

Table 6 Average values of activity concentrations of primordial radionuclides in soils of different countries from Asia

Country (study area)	Activity concentration (Bq kg^{-1})		
	^{40}K	^{226}Ra (^{238}U)	^{232}Th
Armenia (UNSCEAR 2000) [5]	360 (310–420)	51 (32–77)	30 (29–60)
Bangladesh (Rangpur) [46]	1,119	76	119
Bangladesh (Dhaka) [47]	645	73	21
China [5]	440 (9–1,800)	32 (2–440)	41 (1–360)
China/Xiazhuang [48]	672 (442–913)	112 (40–442)	72 (33–88)
Hong Kong [5]	530 (80–1,100)	59 (20–110)	95 (16–00)
India [5]	400 (38–760)	29 (7–81)	64 (14–160)
India/Bangalore [49]	635 (152–1,424)	26 (7–112)	53 (17–99)
Iran [5]	640 (250–980)	28 (8–55)	22 (5–42)
Japan [5]	310 (15–990)	33 (6–98)	28 (2–88)
Jordan (Araba valley) [50]	(19–762)	(19–9)	(14–35)
Kazakstan [5]	300 (100–1,200)	35 (12–120)	60 (10–220)
Malaysia [5]	310 (170–430)	67 (38–94)	82 (63–110)
Syrian [5]	270 (87–780)	20 (13–32)	20 (10–32)
Taiwan [5]	431	30	44
Thailand [5]	230 (7–712)	48 (11–78)	51 (7–120)
World [5]	400 (140–850)	35 (17–60)	30 (11–64)
Asia (present compilation)	486 (129–994)	48 (16–137)	53 (17–109)
Pakistan (present study)	648 (421–996)	45 (32–60)	59 (46–72)

Table 7 Hazard indices and dose rates due to activity concentrations in the soil samples collected from four districts in Peshawar basin of Khyber Pakhtunkhwa, Pakistan

Location	Hazard index		Outdoor dose		Indoor dose	
	Ra$_{eq}$ (Bq/kg)	I$_\gamma$	$\dot{D}_{out}$ (nGy h^{-1})	E$_{out}$ (mSv y^{-1})	$\dot{D}_{in}$ (nGy h^{-1})	E$_{in}$ (mSv y^{-1})
Charsada						
Range	179–237	0.66–0.88	83–112	0.10–0.14	194–262	0.95–1.29
AM ± SD	201 ± 15	0.75 ± 0.74	94 ± 7	0.12 ± 0.01	221 ± 17	1.08 ± 0.09
Mardan						
Range	141–207	0.51–0.76	65–97	0.08–0.12	152–227	0.74–1.11
AM ± SD	171 ± 19	0.63 ± 0.62	79 ± 9	0.10 ± 0.01	185 ± 21	0.91 ± 0.10
Nowshera						
Range	145–205	0.54–0.76	68–97	0.08–0.12	160–227	0.79–1.11
AM ± SD	180 ± 22	0.67 ± 0.66	84 ± 10	0.10 ± 0.01	197 ± 24	0.96 ± 0.12
Peshawar						
Range	139–190	0.52–0.70	65–88	0.08–0.11	152–205	0.75–1.01
AM ± SD	164 ± 13	0.60 ± 0.60	76 ± 6	0.09 ± 0.01	178 ± 14	0.87 ± 0.07
Peshawar Basin						
Range	139–237	0.51–0.88	65–112	0.08–0.14	152–262	0.74–1.29
AM ± SD	180 ± 23	0.66 ± 0.09	84 ± 11	0.10 ± 0.01	196 ± 26	0.96 ± 0.13

The minimum, maximum and the average Ra$_{eq}$ activities of the investigated samples from the four district of Peshawar basin are given Table 7. The soil samples from Charsada district had maximum Ra$_{eq}$ value of 237 Bq kg^{-1}, which was less than the recommended upper limit of 370 Bq kg^{-1}. The H$_{ex}$ is therefore found to be less than unity for the all the studied samples. The minimum

Ra$_{eq}$ value of 139 Bq kg^{-1} is in the soil of Peshawar district. A frequency distribution graph for Ra$_{eq}$ activities for all the samples is also shown in Fig. 3, the trend is towards the lognormal distribution.

The values of gamma index (I$_\gamma$) in the soil samples from Peshawar basin are found in range 0.51–0.88 (Table 7). The minimum value corresponds to the samples from

Fig. 5 External dose rates from soil of some districts of Pakistan along with UNSCEAR median value
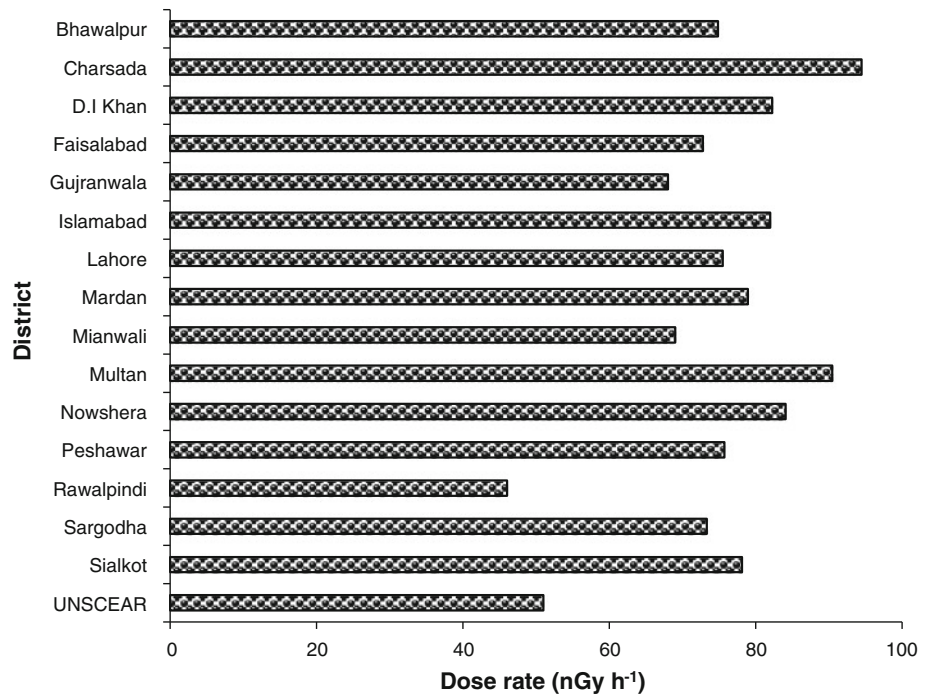
Mardan and the maximum to those from Charsada. None of the samples exceeds its upper limit of 2 as set by the European Commission. Therefore, the soil of the area again was found to be safe and did not pose any serious radiation hazard to the population living in this area.

The external dose rate in air from the soil of the understudy area was calculated using Eq. (8) that ranged from 65–112 nGy h^{-1} with an average value of 84 nGy h^{-1} (Table 7). The minimum value corresponded to the soil of Peshawar and Mardan and the maximum belonged to the soil of Charsada. The mean dose rate is 47 % higher than the corresponding UNSCEAR median value of 57 nGy h^{-1}. This increase was due to the higher average contents of ^{40}K, ^{226}Ra and ^{232}Th in the soil samples of Peshawar basin.

For 15 different districts of Pakistan listed in Table 5, the external dose rates in air from soil were computed and compared in a bar graph shown in Fig. 5. All the regions in comparison have the external dose rate greater than the UNSCEAR median value [5] with the exception of Rawalpindi district which has a value of 46 nGy h^{-1} whereas Charsada district observed to have maximum value of 94 nGy h^{-1}.

Annual effective dose for the inhabitants of the area under investigation was calculated and is given in Table 7. The outdoor annual effective dose range is 0.08–0.14 mSv y^{-1} and with average value of 0.10 mSv y^{-1} which is higher than its respective UNSCEAR median value of 0.07 mSv y^{-1}. For children and infants, these values were about 10 and 30 % higher, in

direct proportion to an increase in the value of the conversion coefficient from absorbed dose rate in air to annual effective dose [5].

The indoor external dose $(\dot{D}_{in})$ calculated for the model room made up of bricks fabricated from the soil of Peshawar basin ranged from 152 to 262 nGy h^{-1} (Table 7), which is higher than the worldwide range 20–200 nGy h^{-1} [5]. The average indoor dose rate in the soil mad dwelling of Peshawar basin is 196 nGy h^{-1} which is two times higher than its worldwide average value of 75 nGy h^{-1} [2].

The effective dose rate (E_{in}) calculated for a room constructed of the soil made bricks of the understudy area are given in Table 7. The average E_{in} varied in range 0.74–1.29 mSv y^{-1} with an average value of 0.96 mSv y^{-1}. The maximum value in the range exceeds the recommended annual limit of 1 mSv for the general public [39].

Conclusions

A study was carried out for the investigation of natural radioactivity in the soil of four districts occurring in the Peshawar basin of Pakistan. Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in soil samples were 648 ± 121 (421–996), 45 ± 7 (32–60) and 59 ± 7 (46–72) Bq kg^{-1}, respectively. Different radiological hazard parameters were derived from the measured activity concentrations of naturally occurring radionuclides. The maximum value of the radium equivalent activity was less than the upper bound

value of 370 Bq kg^{-1}. The value of gamma index was less than its limiting value. The average absorbed dose rate and the annual effective dose for both indoor and outdoor environments were found to be higher than the worldwide values of these indices. However, on the basis of the evaluated hazard indices, no significant radiation health hazard was found in the soil of the investigated area for the population living in Peshawar basin. This investigation has provided base line values for radioactivity in the Peshawar basin of Pakistan.

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