

Measurements of chemical and radionuclide concentrations in the phosphate deposits around Gafsa in Tunisia

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ABSTRACT

Environmental radiation measurements are useful to identify areas of potential natural radiation hazard and assess the human population dose due to terrestrial radiation, particularly in areas of mining activities where enhanced radiation levels are expected to be present. Measurements have been carried out of the concentrations of primordial radionuclides in samples of phosphate layers collected from Gafsa City and its surrounding region in central of Tunisia, Moularaes and Kef Schfayer. The chemical composition in the phosphate samples was also analysed by X-ray diffraction technique (XRD). Measurements of radon concentration levels, indoors and outdoors, were performed in some workplaces situated within the phosphate deposit area using solid state nuclear track detectors. The results show that concentration ranges (minimum to maximum, in Bq .kg⁻¹) of the naturally occurring radionuclides, comprising ⁴⁰K, ²²⁶Ra, ²³⁸U and ²³²Th from Moularaes are 21.6-149.4, 360.9-580.2, 20.3-85.8 and 12.5-70.6 respectively. The corresponding concentrations ranges (Bq.kg⁻¹) from Kef Schfayer are 15.2-28.8, 285.7-447.9, 6.9-24.9 and 26.9-76.4, respectively. The calculated absorbed doses are higher than the global population weighted average. The chemical analysis shows that the phosphate layers are composed of CaO, P₂O₅, SiO₂, Al₂O₃, SO₃ and Fe₂O₃. The concentrations and chemical distributions of heavy metals (Cd, Cr, Zn, Ni, Cu, Cd and U) in Moularaes and Kef schfayer phosphate ores were investigated. The margin of concentrations in ppm of Cd, Cr, Zn, Ni, Cu, Cd, U in Moularayes are 116-209, 74-241, 47-60, 0.66-10.23, 18-54, 112-206.3 respectively, the variation of this heavy metal in ppm in Kef Schfayer are 102-237, 106-176, 33-56, 4.21-13.96, 29-64, 132-168.4, respectively. The radon concentration levels as measured in some workplaces in kef Eddour lounder within the area were found to be within the range of 5 to 130 Bq.m⁻³ and an average value of 23.8 Bq .m⁻³, which are below the ICRP action levels. The results may be useful in the assessment of the exposures and the radiation doses due to naturally radioactive element contents in the phosphate samples.

Keywords: Phosphate rocks, radon measurements, radionuclide, effective dose, dose assessment.

INTRODUCTION

Phosphate rock (PR), in general term, describes naturally occurring mineral assemblages containing high concentrations of phosphate minerals [1]. Most commonly of the apatite group $\{Ca_5(PO_4)_3[F, OH \text{ or } Cl]\}$ [2]. PR can be commercially exploited; either as raw material or after some processing is performed. Phosphate is found as sedimentary, igneous and metamorphic rocks in the earth's crust. Eighty percent of the world phosphate rock production is derived from igneous rocks and their weathering derivatives and the remainder come from residual sedimentary and guano-type deposits. Phosphate deposits are used as raw material for manufacturing of phosphate fertilizer [3], the remainder being used for animal feed additions and industrial applications including detergents and metal treatment [4], and, also as a minor constituent, phosphate is added to many products of daily use such as: soft drinks, vitamins, toothpastes, light bulbs, flame-resistant fabrics, optical glass, safety match heads, cosmetics, shaving cream [5].

Environmental radiation measurements are useful to identify areas of potential natural radiation hazard and assess the human population dose due to terrestrial radiation, particularly in areas of mining activities where enhanced radiation levels are expected to be present.

PR processing is one of the non-nuclear sources of technologically enhanced natural radiation (TENR) that results in the increase of exposure to man from natural radionuclides such as ^{238}U and ^{226}Ra in the particulates emitted from plants [6, 7, 8]. It is known that the main radioactivity of phosphate rock deposit is due to ^{238}U and its decay products [9]. Emanation of radon (^{222}Rn) is associated with the presence of radium and its ultimate precursor uranium in the ground [8]. Also, phosphate mining release toxic metals in the environment such as, Cu, Al, Co, Cr, Fe, Pb, Ni, etc. These metals when present in mining or milling dust are washed out from air through wet deposition but then enter the surface waters through run off and pollute the environment by accumulation in soil and contaminate the food chain [5].

Tunisia is one of the large phosphate producers in the world with a production capacity of more than 10 million tons per year (since the early nineties). Phosphate industry in Tunisia is considered a very developed sector. Phosphorite deposits in Tunisia are located in the north-south Axis and in the Gafsa-Metlaoui region. Gafsa basin is one of the most geologically investigated areas in southern Tunisia [5].

The exposure to workers in the phosphate mine area has not been controlled or monitored. In view of the harmful effects on human health due to the mining and processing of phosphate ore for the manufacturing of agricultural fertilizers, and other chemical products, it is important to analyze phosphate ores for radioelement content and elemental composition, because these products are transported around the world and because of the possible migration of elements from the fertilizers to soil and plants, and via the food chain, to human beings where this may result in health effects [10].

Also detailed chemical characterization of rock deposit is required to check and account for heavy metal content because quantification of these pollutants relative to nutrient value of rock can help in designing and improvement of the chemical process used for production in industry [5].

In the present study, an investigation was carried out to study the chemical and radiological characteristics of phosphate layers from two phosphate deposits of Kef Schfayer and Moularaes located in Gafsa in southern Tunisia in order to estimate the radiation dose received by phosphate workers, two parameters were considered: 1) the external radiation exposure from gamma radiation, and (2) the dose received due to the inhalation of airborne radon.

MATERIALS AND METHODS

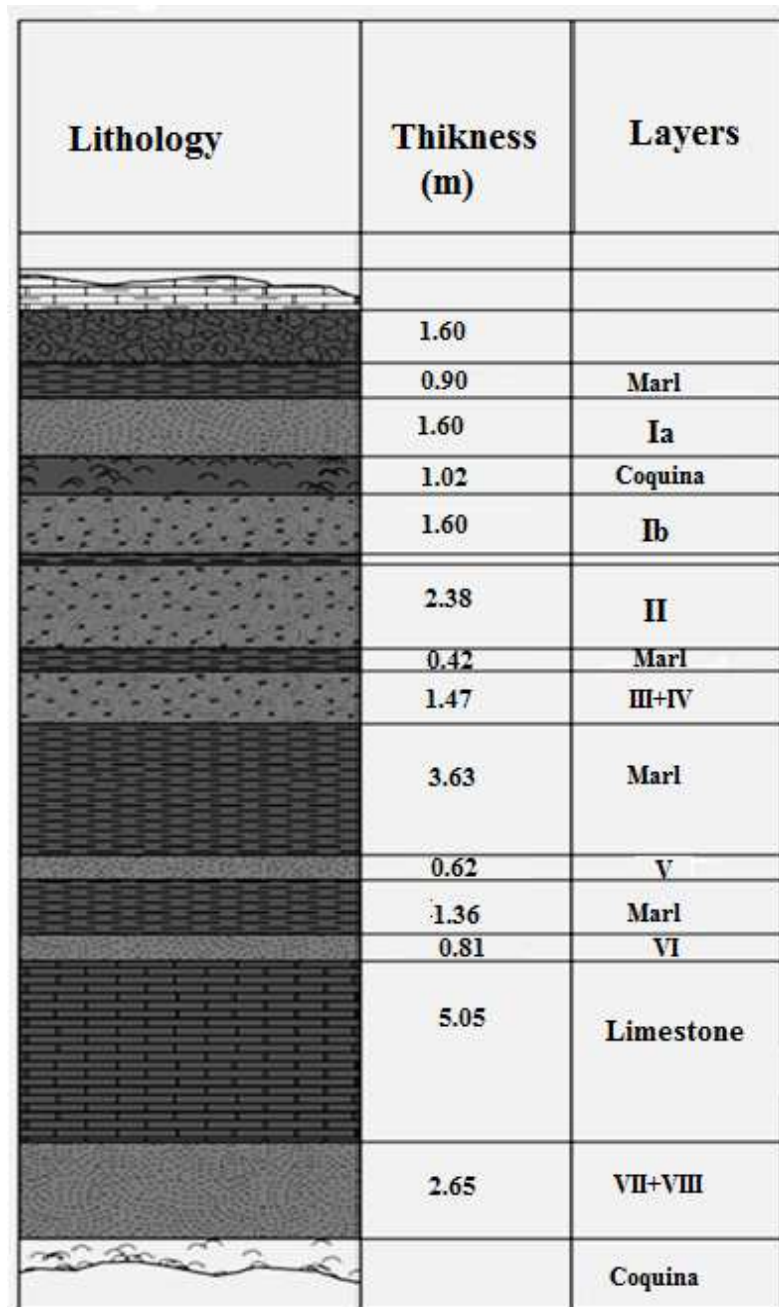
I- Sampling

Phosphate Samples (Ia, Ib, II, III, IV, V, VI, VII, and VIII) from Moularaes deposit and (I, II, III, IV, V and VI) from Kef Schfayer deposit were randomly collected according to the position of workable phosphate layers from bottom to top (Figure 1 and Figure 2). The location map of the phosphate deposits and the places of phosphate sampling are presented in Figure 3 [11].

The samples were crushed with a jaw crusher BB 100 (Retsch, Haan, Germany) and dried at room temperature and

then further crushed with a Mastersizer 2000 (Malvern Instruments, Orsay, France) to pass through a 2-mm test sieves (Retsch, Haan, Germany) for homogenization. The samples were further dried at 105 °C for 24 h in an oven memmert ELU 800 (Memmert, Schwabach, Germany) to ensure the complete removal of moisture.

Dry samples of weight 170±2 g were sealed in gas-tight radon-impermeable cylindrical polyethylene containers (5.5 cm diameter and 5 cm height). These samples were then left for 30 days to allow ²²⁶Ra and progeny to reach radioactive equilibrium.



Legend:

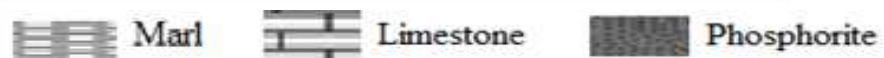
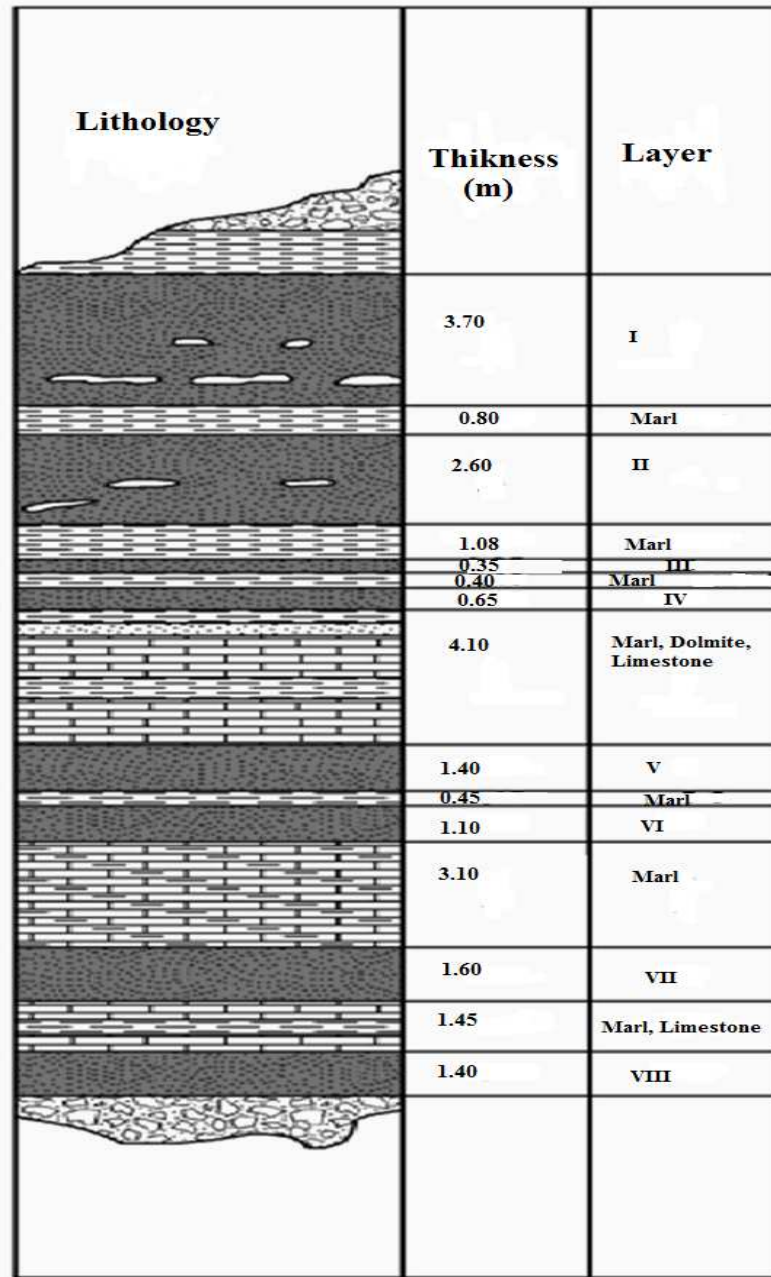


Figure 1: Lithological cut of Moularaes deposit scale (1/200)



Legend:



Figure 2: Lithological cut of Kef schfayer deposit scale (1/200)

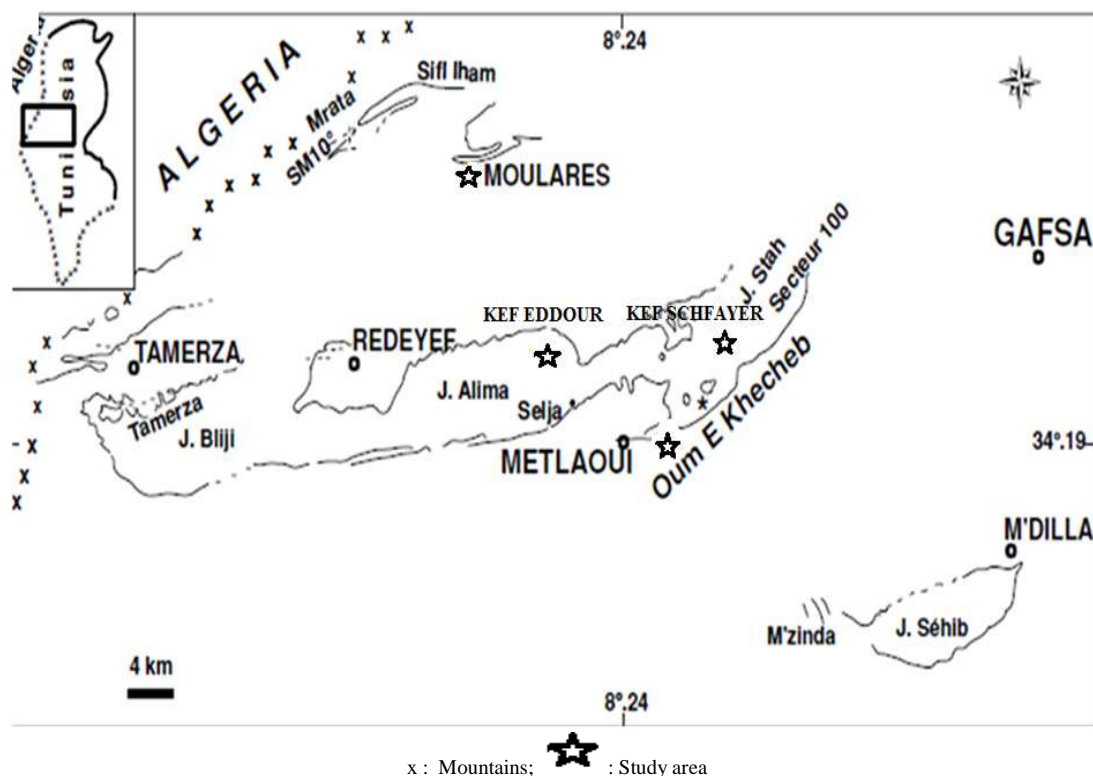


Figure 3: Location map of phosphate deposit in Gafsa Metlaoui region [11].

II- Structural and chemical analysis

The X-ray diffraction (XRD) analysis was carried out for the phosphate samples using a Rigaku D/Max-IIIIC X-ray diffractometer (Rigaku, Tokyo, Japan) with CuK-radiation over the range 10° – 70° with a scan speed $0.2^{\circ} \text{ min}^{-1}$ at room temperature. EDXRF spectrometer (Epsilon5, PANalytical, Almelo, and the Netherlands) was used for chemical analysis of the phosphate samples.

III- Radionuclide measurements

Measurements were performed to determine ^{226}Ra , ^{232}Th , ^{40}K and ^{238}U using a HPGe detector Canberra coaxial P-Type (CANBERRA Industries, Meriden, USA) with a resolution of 2 keV and a relative efficiency of 30% at 1.33 keV. The 609 keV energy line of ^{214}Bi was used to determine the ^{226}Ra activity concentration, whereas, the concentration of ^{238}U was determined from ^{234}Pa gamma lines. For the ^{232}Th activity concentration, 228Ac energy line was used. Calibration of the detection system was performed using a certified multi-gamma source and was controlled by reference materials of International Atomic Energy Agency (IAEA), IAEA 327 and IAEA 375.

1-Radium Equivalent

The gamma radiation hazard due to the natural radionuclides ^{226}Ra , ^{232}Th and ^{40}K was assessed by different radiation hazard indices. The distribution of ^{226}Ra , ^{232}Th and ^{40}K in samples is not uniform. In order to compare the activity concentrations and the radiological effects of phosphate samples, which contain such primordial radionuclides, the radium equivalent activity (Ra_{eq}) as a common index has been used. The index compares the activities of materials containing different amounts of radium, thorium and potassium. The index is based on the estimation that 370 Bq kg^{-1} of ^{226}Ra , 259 Bq kg^{-1} of ^{232}Th and 4810 Bq kg^{-1} of ^{40}K produce the same gamma-ray dose¹² and therefore Ra_{eq} can be written as:

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

Where A_{Th} , A_{Ra} and A_K are the activity concentrations of ^{232}Th , ^{226}Ra and ^{40}K , respectively in Bq kg^{-1} , The maximum value of Ra_{eq} must be less than 370 Bq kg^{-1} in order to keep the external dose to be less than 1.5 mGy.y^{-1} [12].

2- Absorbed and Effective Dose Rate:

The total absorbed dose rate in air ($\text{nGy}\cdot\text{h}^{-1}$) at 1-m above the ground due to the activity concentrations of ^{226}Ra , ^{232}Th and potassium ^{40}K were calculated according to United Nations Scientific Committee on the Effects of Atomic Radiation [13] as :

$$D = 0.0417A_K + 0.462A_{\text{Ra}} + 0.604A_{\text{Th}} \quad (\text{A.2})$$

Where A_{Ra} , A_{Th} and A_K are the activity concentrations in (Bq kg^{-1}) of ^{226}Ra , ^{232}Th and ^{40}K respectively.

To estimate the annual effective dose rate, the conversion coefficient from absorbed dose in air to effective dose (0.7 Sv Gy^{-1}) and outdoor occupancy factor (0.2) are used [13,14] :

$$\text{AED} = D \times T \times F \quad (\text{A.3})$$

where D is the calculated dose rate ($\text{nGy}\cdot\text{h}^{-1}$), T is the outdoor occupancy time ($0.2 \times 24 \text{ h} \times 365.25 \text{ d} = 1753.2 \text{ h y}^{-1}$), and F is the conversion factor ($0.7 \times 10^{-6} \text{ Sv}\cdot\text{Gy}^{-1}$) [13].

Another radiation hazard index called the representative level index I_{yr} is defined from the following formula according to [14, 15] .

$$I_{\text{yr}} = 1/50 \times A_{\text{Ra}} + 1/100 \times A_{\text{Th}} + 1/1500 \times A_K \quad (\text{A.4})$$

Where A_{Ra} , A_{Th} and A_K are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in Bqkg^{-1} , respectively.

3- The external hazard index

The external health hazard index H_{ex} arising from the use of this mineral was determined by employing the formula [16].

$$H_{\text{ex}} = A_{\text{Ra}}/370 + A_{\text{Th}}/259 + A_K/4810 \leq 1 \quad (\text{A.5})$$

Where A_{Ra} , A_{Th} and A_K are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in $\text{Bq}\cdot\text{kg}^{-1}$, respectively.

In addition to external hazard index, radon and its short-lived products are also hazardous to the respiratory organs. The internal exposure to radon and its daughter products is quantified by the internal hazard index H_{in} , which is given by the equation:

$$H_{\text{in}} = A_{\text{Ra}}/185 + A_{\text{Th}}/259 + A_K/4810 \leq 1 \quad (\text{A.6})$$

Where A_{Ra} , A_{Th} and A_K are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in $\text{Bq}\cdot\text{kg}^{-1}$, respectively. The values of the indices (H_{in} , H_{ex}) must be less than unity for the radiation hazard to be negligible¹⁶.

IV- Radon measurements

The LR-115 type II radon dosimeters were used in this survey where 14 workplace locations (offices, laboratories) were covered for indoor radon measurement in the Research Center of phosphate in the Metlaoui region. In addition, another 72 locations in a phosphate mine of Kef Edour region were considered for indoor and outdoor measurements of radon concentrations.

The dosimeters were left in each location above the floor away from walls (at least 10 cm) to provide integrated measurements over a period ranged from 85 to 121 days in three different periods of 2013 (February-May; April-July and July-November).

1- Radon effective dose

In order to investigate the annual mean effective dose H ($\text{mSv}\cdot\text{y}^{-1}$) 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 [13] :

$$H = C \times F \times D \times T \times O \quad (A.7)$$

where C is radon concentration in Bq.m^{-3} , F for equilibrium equivalent concentration (EEC) factor, D for dose conversion factor ($9 \times 10^{-6} \text{ mSv.h}^{-1}$ 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 hours per day at work [17].

RESULTS

I- Chemical analysis

The chemical composition of PR from Moularaes and Kef Schfayer are listed in Table 1. The chemical analysis of phosphate samples revealed that the major elements from the Moularaes phosphate deposit are CaO, P_2O_5 , SiO_2 , MgO, Al_2O_3 , SO_3 and Fe_2O_3 with percentage ranges of (30.9-35.8 %), (17.5 -24.4 %), (5.6-21,3%), (0.56-2.8 %), (0.62-4.03 %), (1.22-6.11 %), and (0.01-0.93 %) respectively.

The major elements from Kef Schfayer contained CaO, P_2O_5 , SiO_2 , MgO, Al_2O_3 , SO_3 , and $\text{Na}_2\text{O Fe}_2\text{O}_3$ with a percentage ranges of (28.61-39.60 %), (22.46-29.19 %), (0.53-6.15%), (0.63-1.04%), (0.76-0.90%), (2.83-4.92%) and (0.21-0.25%) respectively.

Table 1: Chemical analysis of phosphate sample from Moularaes and Kef Schfayer deposits

Phosphate deposits	Layers	CaO %	P_2O_5 %	SiO_2 %	MgO %	Al_2O_3 %	SO_3 %	Na_2O %	Fe_2O_3 %	F %
Moularaes	I a	33.76	24.46	11.31	1.96	4.03	1.56	0.54	0.68	3.64
	I b	30.91	17.53	21.33	2.86	2.97	2.91	1.14	0.93	3.80
	II	35.87	23.01	10.55	2.37	3.64	1.22	BLD	0.01	3.69
	III+IV	33.00	22.56	15.04	1.48	2.37	5.11	1.30	0.74	3.38
	V	35.89	23.87	5.66	0.56	0.62	3.44	0.01	BLD	3.78
	VI	30.14	21.05	18.66	1.50	2.81	6.11	1.15	0.85	3.90
	VII+VIII	35.23	23.59	13.67	2.06	2.48	1.82	0.90	0.52	3.68
Kef Schfayer	I	34.66	22.47	2.23	1.04	0.82	4.92	1.26	0.22	3.25
	II	39.60	26.33	0.53	0.72	0.76	4.12	1.65	BLD	3.43
	III+IV	34.16	22.93	6.15	0.63	0.79	4.90	1.32	0.25	2.56
	V	28.61	29.19	1.92	0.81	0.87	2.92	1.70	0.21	3.32
	VI	38.52	26.69	2.55	0.77	0.90	2.83	1.44	0.22	3.44

BLD: undetectable

In Moularaes the I a, II, III+IV, VI and VII+VIII samples are considered as a rich layers with a P_2O_5 lies between 23 and 23.8%, as a poor layer, we found I-b and V samples with a P_2O_5 ranges between 17.527 and 21.048%. The CaO content in Moularaes layers ranges between 30.135-35.89%, in Kef Schfayer, the CaO ranged from 28.6 to 39.6 %. The concentration of uranium in ppm ranged from 112.3 to 206.5 in Moularaes phosphate layers and from 132.2 to 168.4 in Kef Schfayer phosphate layers. MgO content in Moularaes samples ranges between 0.5 to 2.8%, while in the Kef Schfayer samples the MgO lies between 0.6 and 1%.

The elemental analysis of 12 layers of PR from Moularaes and Kef Schfayer (Table 2) showed that the trace metal contents of the PR analyzed varied greatly.

Two groups of trace metals may be easily identified according to their concentrations. The first group consists of trace metals present in relatively high concentrations: Cr, U and Zn, the range of concentrations (ppm) in Moularaes deposit were: Cr (116-209), U (112-206), Zn (74-241), in Kef Schfayer, the margin of concentrations in ppm was: Cr (102-237), U (132-168.40) and Zn (106-168.40).

The second group consists of trace metals present in moderate concentrations: Cd and Ni. The ranges values expressed in ppm were: Cd (18-54), Ni (47-62) in Moularaes, whereas the concentrations ranges in ppm in Kef schafyer were: Cd (29-64), Ni (42-56).

Table 2: The elemental analysis of phosphate samples from Moularaes and Kef Schfayer deposits

Phosphate deposit	Layers	Cr ppm	Zn ppm	Ni ppm	Cu ppm	Cd ppm	Cl ppm	U ppm
Moularaes	Ia	202	241	52	9.68	18	996	150.91
	Ib	191	238	47	10.23	45	923	145.16
	II	204	156	56	9.36	25	943	156.73
	III+IV	192	93	62	8.25	37	56	112.34
	V	209	123	49	5.37	54	950	206.53
	VI	186	75	60	1.84	23	510	125.30
	VII+VIII	116	74	56	0.66	34	918	158.87
Kef Schfayer	I	168	135	38	13.22	60	1436	161.18
	II	173	142	42	12.56	64	1512	139.05
	III+IV	102	106	26	4.43	29	356	132.23
	V	237	176	33	13.96	35	1455	160.30
	CVI	195	108	56	4.21	50	1487	168.40

The corresponding values of the third group, which consisted of trace metals present in relatively small concentrations, were Cu concentrations varied from 0.66 to 10.26 ppm in Moularaes deposit and from 4.21 to 13.96 ppm in Kef schfayer deposit. The concentrations of F and Cl in Kef Schfayer and Moularaes phosphate samples have a certain similarity.

II- Radioelement analysis

The results of radioelement components of the phosphate samples layers collected from Moularaes and Kef Schfayer deposit are presented in Table 4.

The activity concentration of the naturally occurring ^{226}Ra , ^{232}Th , ^{40}K and ^{238}U from Moularaes are with the ranges of 360.9-580.2 Bq.kg⁻¹, 12.5-70.6 Bq.kg⁻¹, 21.6-149.4 Bq.kg⁻¹ and 20.3-85.8 Bq.kg⁻¹ respectively.

Table 4: Activity concentration in (Bq/Kg) of ^{226}Ra , ^{232}Th , ^{40}K , ^{238}U and radiation hazard parameters in phosphate samples from Moularaes and Kef Schfayer deposit

Phosphate deposit	Layers	^{40}K (Bq.kg-1)	^{226}Ra (Bq.kg-1)	^{232}Th (Bq.kg-1)	^{238}U (Bq.kg-1)	R_{eq} (Bq.kg-1)	D (nGy.h-1)	HE (mSv.y-1)	I _{yr}	H _{in}	H _{ex}
Moularaes	I a	149	539	69	21	644	297	0.4	4.4	2.5	1.7
	I b	36	492	13	19	512	236	0.3	3.4	2.4	1.4
	II	26	574	71	26	671	309	0.4	4.6	2.3	1.8
	III+IV	35	361	49	15	429	198	0.2	2.9	3.0	1.2
	V	24	526	30	19	568	262	0.3	3.8	2.7	1.5
	VI	23	580	31	29	625	288	0.4	4.2	3.3	1.7
	VII+VIII	22	562	13	29	580	268	0.3	3.9	3.4	1.6
Kef Schfayer	I	86	457	76	18	566	261	0.3	3.9	3.2	1.5
	II	57	286	28	7	327	151	0.2	2.2	3.1	0.9
	III+IV	36	448	27	25	487	225	0.3	3.3	2.2	1.3
	V	41	400	31	16	445	205	0.3	3.0	1.7	1.2
	VI	20	381	34	16	428	197	0.2	2.9	2.5	1.2

The results from Kef Schfayer of ^{226}Ra , ^{232}Th , ^{40}K and ^{238}U are with the ranges of 285.6-447.9 Bq.kg⁻¹, 26.9-76.4 Bq.kg⁻¹, 15.2-28.8 Bq.kg⁻¹ and 6.9-24.9 Bq.kg⁻¹, respectively. The R_{eq} from Moularaes and Kef Schfayer samples ranged from 428.6 to 670.7 Bq.kg⁻¹ and from 327.1 to 565.6 Bq.kg⁻¹ respectively.

In order to calculate the dose rate in air for the phosphate samples collected from Moularaes and Kef Schfayer area, equation (2) was used. The results are shown in Table 4, the dose rate ranged from 197 to 308.5 (nGy. h⁻¹) with a mean average of 265.4 (nGy.h⁻¹) in Moularaes areas and from 151 to 260.7 (nGy.h⁻¹) with a mean average of 207.8 (nGy.h⁻¹) in Kef Schfayer areas. The annual effective dose rates were calculated with equation (3), the values obtained (Table 4) varied from 0.2 to 0.4 mSv.y⁻¹ with an average of 0.2 mSv.y⁻¹ in the samples from Moularaes and a range of 0.2 to 0.3 mSv.y⁻¹ in Kef Schfayer samples with an average of 0.1 mSv.y⁻¹.

The external radiation hazard (H_{ex}) and the internal radiation hazard (H_{in}) was calculated with the equation (5) and (6). The values in Table 4 of H_{in} in Moularaes and Kef Schfayer samples ranged from 2.3 to 3.4 and from 1.7 to 3.2, respectively. Also in Moularaes and Kef Schfayer samples the values of H_{ex} ranged from 1.2 to 1.8 and from 0.9 to

1.5, respectively. The $I_{\gamma r}$ in Moularaes and Kef Schfayer ranged from 2.9 to 4.6 and from 2.2 to 3.9, respectively.

Taking the indoor occupancy factor of 0.8 and a conversion factor of 0.7 Sv.Gy^{-1} to convert the γ -ray absorbed dose to effective equivalent for workers (that is, for a working period of 2937 h in a year) [18], the above-mentioned dose rate (Table 5) corresponds to an annual effective dose of $0.3\text{-}0.5 \text{ mSv.y}^{-1}$ in Moularaes deposit and $0.2\text{-}0.4 \text{ mSv.y}^{-1}$ in kef Echfayer. The calculated external γ -radiation dose received by the workers of the phosphate mines are ranged between 1.9 -2.5 % in Moularaes, and varied from 1.2 to 2.1 % in Kef Echfayer.

Table 5 : Annual effective dose (mSv y^{-1}) received by workers in phosphate mine deposits of Moularaes and Kef Echfayer

Phosphate deposit	Layers	H_E (mSv y^{-1})	Dose ^a (%)
Moularaes	Ia	0,5	2,4
	Ib	0,4	1,9
	II	0,5	2,5
	III+IV	0,3	1,6
	V	0,4	2,2
	VI	0,5	2,4
	VII+VIII	0,4	2,2
Kef Schfayer	I	0,4	2,1
	II	0,2	1,2
	III+IV	0,4	1,9
	V	0,3	1,7
	CVI	0,3	1,6

^a Calculated external g-radiation dose received by the workers of the phosphate mines, the world allowed dose of 20 mSv/y (ICRP-60, 1990) for workers.

TABLE A.6: Mean value of radon Concentration and annual effective doses in Kef Eddour workplaces (Continued)

location	site	Site description	workers	Duration of exposure (day)	Average radon concentration (Bq/m^3) ^a	Annual effective dose mSv/y
Handling area (Conveyors)	12	opened	2-6	106	6 ± 2	0.07
	18			106	10 ± 3	0.11
	51			121	23 ± 7	0.25
	52			121	22 ± 6	0.24
	54			121	12 ± 4	0.13
	55			121	12 ± 4	0.13
	56			121	17 ± 5	0.19
	57			121	18 ± 6	0.20
	58			121	118 ± 4	1.30
	60			121	17 ± 5	0.19
	79			85	5 ± 3	0.06
	Size reduction area (dryin, grinding,screening)			13	opened	3-6
14		106	<8	-		
15		106	<8	-		
33		106	5 ± 2	0.06		
34		106	6 ± 2	0.07		
35		106	9 ± 4	0.10		
37		106	11 ± 4	0.12		
38		106	6 ± 2	0.07		
39		106	<8	-		
40		106	9 ± 3	0.10		
41		106	9 ± 3	0.10		
53		121	11 ± 4	0.12		
Washing area		42	opened	3		
	59	85			11 ± 6	0.12
	66	119			<8	-
	67	119			8 ± 3	0.09
	68	119			<8	-
	69	119			4 ± 2	0.04

III- Radon

The measurement was effected in the beneficiation and concentration plant of phosphate in Kef Edour region. The places are handling area, size reduction area, washing area, filtration area, flotation area, water basin, screening and

dewatering area, drying area, storage area of buildings. Places in cited for the data of indoor and outdoor radon measurement in Tables.6 and Table 7 are more than three significant places justified.

TABLE A.6: Radon Concentration (Bq/m³) and annual effective doses in Kef Eddour workplaces (Continued)

location	site	Site description	workers	Duration of exposure (day)	Average radon concentration (Bq/m ³) ^a	Annual effective Dose mSv/y
Filtration area	32	Opened	9	106	<8	-
	43			106	<8	-
	44			106	9±4	0.10
	45			106	<8	-
	20			106	<8	-
flotation area	21	Opened	6	106	<8	-
	24			106	<8	-
	25			106	<8	-
	26			106	31±8	0.34
	27			106	6±2	0.07
	29			106	7±3	0.08
Water basin	19	Opened	3	106	<8	-
screening and dewatering area	11	Opened	6	106	<8	-
	16			106	<8	-
	17			106	<8	-
	28			106	6±2	0.07
	46			106	<8	-
	47			106	6±2	0.07
	48			106	22±6	0.24
	49			106	10±3	0.11
	50			106	10±4	0.11
	64			119	17±5	0.19
	65			119	18±6	0.20
	70			119	9±3	0.10
	71			119	10±4	0.11
Drying area	72	Opened	3	119	11±4	0.12
	73			119	7±3	0.08
	74			119	13±4	0.14
	75			119	8±3	0.09
	76			119	5±2	0.06
	77			119	7±3	0.08
Storage area	78	opened	10	85	23±10	0.25
Room of under Electric station	61	closed	3	119	14±5	0.15
	62			119	22±6	0.24
	63			119	34±9	0.38
Pumps room	22	closed	30	85	<8	-
	23			106	21±9	0.23
workshop	1	Closed	6	106	42±10	0.46

Table 7: Radon concentration and annual effective doses in workplaces of Research Center in Metlaoui

location	site	Site description	workers	Duration of exposure (day)	Average radon Concentration (Bq.m ⁻³) ^a	Annual effective dose (mSv.y ⁻¹)
Crushing room	81	closed	4	91	12±6	0.13
	84			102	11±4	0.12
	90			102	8±3	0.09
office	82		1	91	112±33	1.24
Mineralogy room	83		11	91	78±25	0.86
	87			102	38±11	0.42
	92			102	58±15	0.64
Drying oven room	85		19	102	27±9	0.30
Transformation room	86		3	102	70±18	0.77
Rock room	88		08	102	59±15	0.65
Balance room	89		19	102	52±14	0.57
Diffraction-X laboratory	91		3	102	330±63	3.64

^a Mean results from three experiments.

The values of the outdoors radon in Kef Edour varied from 5 to 118 Bq m⁻³, with an average of 13.80 Bq.m⁻³. We found in site (14-15-39-66-68-32-43-4520-25-19-11-16-17-46) that the concentration of Ra was less than 8 Bq.m⁻³. The corresponding annual effective dose in this opening site varied from 0.04 to 1.31 mSv.y⁻¹. Whereas, the indoor radon concentration determined in same closed workplaces in kef Edour such as control Room of electric station, pump room and in the workshop of maintenance levels varied from 14±5 to 42±10 Bq.m⁻³. The annual effective dose was found between 0.15 and 0.46 mSv.y⁻¹. The indoor levels of radon in research center of phosphate in Metlaoui were determined in Table 7. The sites were crushing room, office, Mineralogy room, Drying oven room, Transformation room, Rock room, Balance room, diffraction X laboratory, where the concentration varied from 8±3 to 330±63 Bq.m⁻³. The annual effective dose calculated in the research center ranged from 0.09 to 3.64 mSv .y⁻¹.

The radon concentrations in the present study were obtained in three different periods February-May, April-July and July-November 2013, and the mean radon concentration level values are 37.4, 29.9 and 17.9 Bq m⁻³ respectively.

DISCUSSION

I- Chemical analysis

The phosphate samples were chemically analyzed to quantify the major and trace elements, in order to define the potential damage that such wastes can cause to the environment. Phosphate ores are divided into three groups based on their P₂O₅ content: low-grade ores (12– 16% P₂O₅), intermediate-grade ores (17–25% P₂O₅) and high-grade ores (26–35% P₂O₅) [3]. Deposits that are mined and processed to give about 28–38% P₂O₅ are considered economically commercial phosphate deposits [19].

The P₂O₅ content in Moularaes samples ranges from 17.5 to 24.5 % and in Kef Schfayer the P₂O₅ ranges from 22.5 to 29.2%. This wide range of P₂O₅ content, in the studied samples, is mainly due to the admixture of non-phosphatic minerals such as quartz, calcite and dolomite [7].

Heavy elements was one of the deciding factors for the quality of phosphate resources, which does not have any standard permissible limit because the maximum allowable content depends on soil characteristics, irrigation water quality, crop type, etc [5].

The data shows that Ni and Cr concentration are relatively higher in Kef Schfayer phosphate ore, whereas, Cd, Cu, Zn and U are higher in Moularaes phosphate ore. Concentrations of F and Cl in Kef Schfayer and Moularaes phosphate have a certain similarity. The amounts of these hazardous elements vary widely not only among various phosphate rock sources but also even in the same deposit [22]. F has beneficial effects on teeth at low concentrations in drinking water, but excessive exposure to fluoride in drinking water and/or from other sources, can adversely affect human health [23]. Exposure to dust containing fluoride may make a contribution to the induction of sister-chromatid exchange [24]. Much attention has been given to Cd, probably because it represents the most harmful heavy metal to human health. In general, the average Cd contents of PRs range from 5 to 100 mg.kg⁻¹; however, for specific PR deposits, the ranges vary from 4 to 109 mg.kg⁻¹ in Australian PR, from 3 to 15 mg.kg⁻¹ in Florida PR, and up to 130 mg.kg⁻¹ in western United States PR [25].

According to the United States Environmental Protection Agency (USEPA) [20], phosphate rock contains between 30 and 200 ppm of Uranium where a support of our results.

Therefore, knowledge of the concentration of trace and non-trace elements in PRs is essential for studies involving soil fertility trials and fertilizer-use efficiency.

The concentration of the element in phosphate rock may be safe from an agricultural point of view, Soils contaminated with heavy metals are a threat to human and ecosystem health [20], as far as human beings are concerned they are exposed to heavy metals from various pathways: inhalation and ingestion of heavy metals from phosphate rock dust, drinking of heavy metal contaminated water as a result of mining, milling, manufacturing and disposal processes and eating of heavy metal affected food etc [5].

Dust is generated and dispersed into phosphate mine air through different production processes, from phosphate rocks, the heavy metals get transported to the environment as an integral part of the suspended sediments [26]. Such dust may play very important role in the atmosphere having significant influence on human health, global warming,

climate change, radiative forcing, visibility, and cloud formation [27]. In order to highlight the relation between the phosphate rocks and the dust in the Metlaoui region, we reported in the Table 8, the comparison of heavy metals of phosphate rocks and dust, we conclude that all the analyzed metals were found enriched in the dust compared to the elements in phosphate rocks, if we consider dust and soil having the same origin, it must have the same elemental composition but the observed difference suggested that chemical characteristics of suspended soil were significantly modified in the atmosphere as the dust particles interacted with atmospheric pollution [28].

TABLE 8: Heavy metals in phosphate rocks and phosphate dust from kef Echfayer and Metlaoui

Heavy metals	Phosphate rocks Kef Echfayer	Phosphate dust Metlaoui
Cd (ppm)	29-64	49-67
Ni (ppm)	42-56	57-60
Cu (ppm)	4.21-13.96	47-170
Zn (ppm)	106-176	300-367
Cr (ppm)	102-237	183-277

The phosphate dust, has the greatest probability of interaction with the human beings, several clinical and epidemiological studies have shown an increased incidence of impairment of respiratory and a prevalence of respiratory symptoms among miners in a phosphate deposit [29].

Phosphate rocks are sources of heavy metal transport on global scale and should be considered in metal transport assessments, ecosystem studies, land-use evaluation, and environmental assessments [25].

II- Radioelement analysis

The radiological impacts of technologically enhanced natural radiation sources, especially phosphate mining and processing, are of great interest [9]. Phosphate deposits throughout the world contain uranium and thorium as natural constituents of the ore. When these naturally occurring radionuclide and their radioactive daughters are underground and covered by overburden, they present no important impact on the biosphere except for that which might arise from leaching into ground waters. However, mining and processing of the phosphate deposits remove this protective overburden and offer the opportunity for redistributing the radioactivity [30]. Dispersal of these materials throughout the environment could increase radiation exposure to the public [30]. The radioactivity of phosphate rock varies regionally, and within the same region the radioactivity of the material varies widely from deposit to deposit [20].

The concentration of ^{232}Th is found to be higher than those published data from Egypt (16 Bq kg^{-1}), Morocco (5 Bq.kg^{-1}), Syria (14 Bq.kg^{-1}) and Turkey (18 Bq.kg^{-1}), the levels of ^{40}K are found to be higher than the concentration measured on phosphate rock samples from some places such as Morocco (5 Bq.kg^{-1}) and Syria (14 Bq.kg^{-1}) [2]. However the concentration of ^{238}U is found lower than the results published for phosphate rocks from Sudan, USA, Tanzania and Egypt. A typical concentration of ^{238}U in sedimentary phosphate deposits as reported for a worldwide is 121 mg/kg (1500 Bq.kg^{-1}) with a range of $30\text{--}260 \text{ mg/kg}$ ($372\text{--}3224 \text{ Bq.kg}^{-1}$) [31].

The composition of ^{226}Ra , ^{232}Th and ^{40}K in PR samples is not homogeneous, and thus the contribution of these radionuclides in terms of exposure to radiation radium equivalent activity has been defined by the equation (1). All the Ra_{eq} values of the samples except for the Sample (II) from kef Schafayer are higher than the reference value of 370 Bq kg^{-1} [15]. Most phosphate is mined in an open-pit or strip mining process, in order to reach the phosphate rock; the overburden and a second layer (called the leach zone) have to be removed. The leach zone has generally a higher concentration of ^{226}Ra , than the overburden and it after wards frequently placed at or near the surface, resulting in increased ^{226}Ra concentrations. The subsequent radon exhalation rate from phosphate regions depends on land reclamation practices.

In the case of occupational exposure, it is reported that the annual effective dose to workers who handle phosphate rocks during industrial operation is $200 \mu\text{Sv y}^{-1}$ [31]. It is well known that the most significant exposure pathways for those workers are the internal dose due to radon and dust inhalation during mining activities [9].

The major source of the total air absorbed dose rate and the annual effective dose in the study area is the Ra versus Th originating from the mine site and the ^{40}K that is naturally found in regional rocks [32], ^{238}U and its progenies contribute mainly to the radioactivity of Kef Schfayer deposit. The ^{238}U and ^{232}Th have relatively low activity

concentrations; their contribution to external exposure during mining processing is generally low [33]. The calculated external γ -radiation doses received by the workers of the phosphate mine are far below the world allowed dose of 20mSv/y for radiations workers [32].

The contribution of dose due to inhalation of radioactive air-borne dust particles and Rn-daughters in the mine along with the external γ -radiation may not exceed the allowed prescribed limits because all mines in areas under investigation are opencast mines [34].

The ICRP-60 (1990) recommends that any exposure above the natural background radiation should be kept as low as reasonably achievable -ALARA- but below the individual dose limits, which for radiation workers averaged over 5 years is 100 mSv.y⁻¹ and for members of the general public is 1 mSv.y⁻¹ [35].

The above results may indicate that the phosphate rocks from Moularaes and kef Echfayer have low radioactivity content in phosphate rock of sedimentary origin resulting in minor radiation dose and environmental impacts through processing. Also, we can conclude that the radiation dose to a member of the public resulting from the use of Moularaes and kef Schfayer's phosphate rocks is negligible compared to the average annual effective dose from natural sources (2.4 mSv.y⁻¹), even under a worst case scenario assuming the complete accumulation of radionuclides in soil over many years [34].

However, because of the presence of small amounts of radionuclides, such as ²²⁶Ra, USEPA has imposed severe restrictions on the use of phosphogypsum [20].

III- Radon

It is well known that the most significant exposure pathways of phosphate mine workers are the internal dose due to radon and dust inhalation during mining activities [34].

Exploitation of the Gafsa phosphate mine is done by open-cast mining. Workers at the mine are likely to be affected by direct external radiation from the rock phosphate and through inhalation of dust from the mine. Measurements of concentration levels of indoor and outdoor radon were performed in different sites of exploitation of the Gafsa phosphate mine.

From our results, it seems that Kef Edour deposits have the low activity levels of exploited phosphate rocks and relatively the minimum radiological dose and environmental impacts through processing. Also, the public resulting from the use of kef Edour Beneficiation plant is negligible compared to the average annual effective dose from natural sources (2.4 mSv.y⁻¹), even when assuming the complete accumulation of radionuclide in soil over many years [9]. The number of workers engaged in the operation of concentration and beneficiation of phosphate rocks are normally conducted 24 hours per day, 7 days per week, and three 8-hour shifts facility, and they have generally not been working in "restricted areas" and these encountered were much less than those noted above [26]. This will require a detailed survey to identify the population at highest risk and situations with the potential to give high radiation exposures and doses [36]. In the research center of Metlaoui, rooms are utilized mostly for stores the samples of phosphate and to prepare them to the physicochemical analysis in the laboratory like the diffraction X laboratory where we measure a high concentration of radon 330 Bq m⁻³, and most of the time that remains closed. The difference of the measured concentration between the seasons could be due to different ventilation condition of the dwellings, the geochemistry of the soil beneath the dwellings [18] and also could due to the fact that non-residential buildings remains closed after the hours working and have poor ventilation [37]. The 1999 Report of the National Academy of Sciences' Committee on the Biological Effects of Ionizing Radiations (BEIR) IV, There is considerable evidence to show that excessive radon levels in some mines cause lung cancer in miners, alpha particles from the decay of radon progeny that are deposited in the lungs cannot reach any other organs, so it is likely that lung cancer is the only potential important cancer hazard posed by radon in indoor air [38]. Inhalation of radon and its short-lived decay products constitutes the most important occupational exposure of workers in mines [39]. The radon daughters are solid particles and when they are inhaled they release radiation (alpha, beta) into the lungs, which can potentially cause cancerous cell growth (in the lungs, epidemiological results from case-controlled extrapolation of radon-exposed underground miners attributed a considerable amount of lung cancers to radon gas [38]. Different reference levels have been recommended by different countries for indoor ²²²Rn concentrations.

ICRP recommends a maximum limit of 600 Bq.m⁻³, however the measured values are lower than the action levels

recommended by the ICRP (200- 600 Bq m⁻³) [18].

One of the main concerns of PG is the enriched amount of the radionuclide, ²²⁶Ra, the parent isotope of ²²²Rn, which further decays to produce Radon gas (²²²Rn). ²²²Rn has a short half-life of 3.8 days and intense radiation capacity. Upon decay of the radon gas, alpha particles are emitted, which are known to cause significant damage to internal organs [40]. The USEPA, therefore, classified PG as a “Technologically Enhanced Naturally Occurring Radioactive Material” (TENORM) [40].

EPA has determined that PG can be used in unlimited quantities in agriculture as long as its ²²⁶Ra content does not exceed 10 PicoCuries per gram (pCi/g) [40].

CONCLUSION

An environmental assessment has been carried out in the region of Gafsa where phosphate mines exist. The study involves chemical and radionuclide analysis for samples collected from the region and radon measurements in indoors and outdoors within the open area and its buildings.

The results of the chemical characterizations of the phosphate layer samples revealed that major compounds from the Moularaes and kef Schfayer phosphate deposit are CaO, P₂O₅, SiO₂, MgO, Al₂O₃, SO₃, Na₂O and Fe₂O₃.

Natural radioactivity levels in phosphate samples from the Moularaes and Kef Schfayer gisement have been measured using gamma-spectrometry system. Observation shows that the layer number I from Moularaes and kef Schfayer presents the highest activities of ²²⁶Ra, ²³²Th and ⁴⁰K. The mean value of Req, I_{vr}, Hint and H_{ext} in Moularaes and Kef Schfayer phosphate samples are (575.3 and 450.5 Bq kg⁻¹), (3.88 and 3.05), (2.78 and 2.5), (1.55 and 1.2) respectively. The absorbed dose rates due to ⁴⁰K, ²²⁶Ra and ²³²Th, in phosphate samples from Moularaes and Kef Schfayer areas varied in the range 197.5-308.9, 151.0-260.7 nGy h⁻¹ respectively. These values are higher than the global population weighted average indoor absorbed dose rates.

The radon measurement in kef Edour and Metlaoui workplaces show that values vary from 5 to 118 Bq m⁻³ and from 3 to 330 Bq m⁻³ respectively, majority of which are below the ICRP action levels. The results may be useful in the assessment of the exposures and the radiation doses due to naturally radioactive element contents in the phosphate samples.

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