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Radiological and Mineralogical Studies on some Selected Farm Soils and Phosphate Fertilizers

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Abstract: Recently, using chemical fertilizers, especially phosphates for high productivity of crops increases soil contamination by radionuclides. Soil samples were collected from three governorates (El Sharqia, El Giza, and El Fayoum), and the used fertilizers are represented by superphosphate and phosphogypsum. All these samples were analyzed radiometrically for radionuclides determination (U, Th, Ra in ppm & K in percent) and investigated mineralogically. The concentration of radionuclides in various governorates is lower than the permissible international levels, suggesting unhazardous limits. A significant concentration of radioelements was found in El Sharqia governorate on average, 1.3 ppm for uranium and 5.94 ppm relative to the others. This could be related to the presence of clay minerals montmorillonite-chlorite and kaolinite with gypsum and associated minerals such as rutile and quartz. The radioelements contents in El Giza soil, average uranium (1.03 ppm) and thorium average (4.83 ppm) may be revised to its adsorption on clay mineral kaolinite and montmorillonite. Fayoum soil samples average uranium are 0.66 ppm and thorium 4.83 ppm and characterized by the presence of clay minerals (kaolinite, Chlorite-vermiculite-montmorillonite) with zirconium silicate mineral. The activity concentrations of uranium and radium in all superphosphate samples were higher than the worldwide average, whereas the activity concentrations of thorium and K-40 in most samples were lesser. Phosphogypsum samples have uranium and thorium contents less than the superphosphate fertilizer but with higher radium and potassium contents. The notable high radium concentration in phosphogypsum could be related to its precipitation with calcium and Ba as Ra sulfates.

Keywords: Pharm soils, phosphate fertilizers, radioactivity, radioelements.

1 Introduction

In general, uranium and its decay products are present in significant levels in sedimentary rock phosphates due to the rock-forming process, Uranium is dissolved in the form of uranyl complexes in seawater and concentrated in the course deposits. [1],[2]. Because of the usage of fertilizer, natural radioactivity in the soil varies from place to place.

It is the primary cause of radiation caused by humans in the soil. [3]; [4]; [5]; [6]; [7]; [8]. To increase crop productivity, the application of various agricultural fertilizers has become increasingly important. [9]; [10]; [11]; [12]. the wet reaction of phosphate rock with concentrated sulphuric acid, the phosphate fertilizer was obtained as the final product, phosphoric acid and dehydrated calcium sulfate (phosphogypsum) as by-products. Phosphoric acid is the essential content for single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP), [13], [14]. A calcium sulfate precipitate is created during this process, called phosphogypsum, as a by-product, which is stocked and considered waste due to its impurities. During the process, the produce is filtered off and pumped as slurry to nearby ponds, where it stays for a period sufficient to allow complete deposition. A secondary product of the production of acidified fertilizers gypsum, has been recently used. Agricultural gypsum, which arises from phosphoric acid, is composed of calcium, sulfur, and water in varied concentrations. This product is used to supply calcium and sulfur to the deeper.

High technology is applied in modern agriculture to increase productivity, so chemical fertilizers result in high productivity. However, the presence of radionuclides in phosphatic fertilizers [15]; [16]; [17]; [18]; [19]. The effects on the environment and the consequences are still unknown. Generally, the specific activities of natural 238U series radionuclides in phosphate fertilizers are based on their contents in the phosphate ore raw material that was used. Geological origin (volcanic, sedimentary, or

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biological origin) causes diversity in Radioactivity levels in phosphate ores, where 238U and its decay products tend to be raised in phosphate deposits of sedimentary origin due to the assemblage of dissolved uranium, in the form of uranyl complex, when the phosphate rocks were being formed in the seawater. A typical concentration of 238U in sedimentary phosphate deposit is 1500 Bq/kg [20]; [21].

The application of plant nutrients, including phosphate fertilizers, has increased significantly. More than 30 million metric tons of phosphate fertilizers are annually consumed worldwide, which increases crop production and land rehabilitation [22]; [23].

This work aims to evaluate the radionuclide distribution and discuss their mobility in the studied soils and fertilizers.

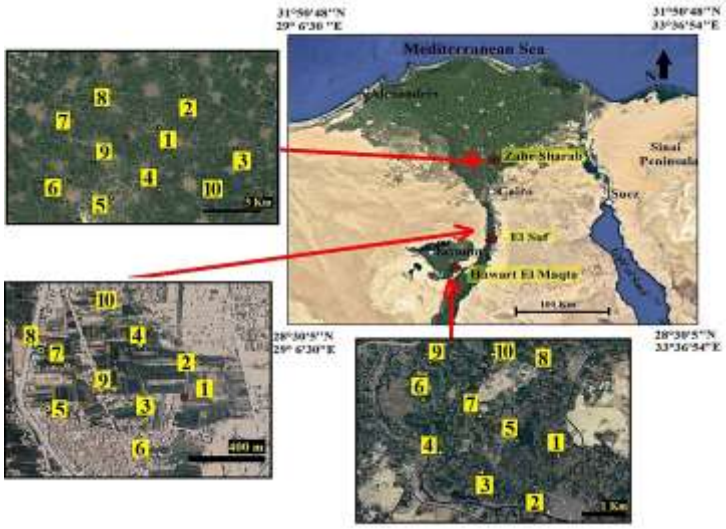

Fig. 1: Landsat images show the location of the studied area and the locations of sample sites.

2 Experimental

2.1 Study Area

The studied sites are located in three governorates of the Nile Delta. The first site (Zahr Sharab) lies approximately 40 km2 in the northern of Greater Cairo at El Sharqia governorate, the second site (Suf) is at Giza governorate in the southern part of Greater Cairo, whereas the third location (Hawarat El Maqata) fits on El Fayoum governorate south of Greater Cairo by nearly 80 km^2 (Fig. 1). In the present practice, replacing nutrients in the soils and consequently supplying substances to reach high productivity is by the application of chemical fertilizers, mostly superphosphate and gypsum. Seven samples were gathered from both superphosphate and gypsum from those fertilizers used in the nutrition of the studied soils.

2.2 Soil Sampling

A total of thirty samples were collected from the various sites based on a well-constrained Global Positioning System (GPS) to access the sampling sites accurately (Fig. 1). The samples were collected at depth (15-30 cm) (Table

2.3 Soil Sampling

A total of thirty samples were collected from the various sites based on a well-constrained Global Positioning System (GPS) to access the sampling sites accurately (Fig. 1). The samples were collected at depth (15-30 cm) (Table 1). They were collected in sealed polyethylene bags using a clean stainless-steel shovel to avoid any cross-contamination.

2.4 Analytical Techniques

The collected samples were sieved into three fractions: >800µm, 800µm-63µm and <63µm. The size fraction ranging between 800µm-63µm for each sample was subjected to heavy liquid separation using bromoform solution (sp. gr. 2.81 g/cm3) to separate the heavy minerals. The heavy fractions that resulted from the bromoform separation were subjected to separate their magnetite content using a hand-magnet. The residue fractions were subjected to magnetic fractionation using Frantz Isodynamic Magnetic Separator (Model LB 1) under the following conditions: transverse slope 5°, longitudinal slope 20° and step of current = 0.2, 0.5, 1.0, and 1.5 amps. The picked mineral grains were analyzed by X-ray diffraction (XRD) technique for mineral

identification. These analyses were carried out in the laboratories of the Nuclear Materials Authority (NMA), Cairo, Egypt.

Clay fractions were separated from soil samples after the pretreatment for the removal of organic matter, carbonates, gypsum, and free iron oxides according to [24]. The clay fractions were separated by the method of sedimentation and decantation at the suitable sedimentation times according to the temperature and viscosity at a standard depth. Oriented clay samples were prepared from the separated clay as Mg-saturated air-dried, Mg-saturated glycerol solvated, K-saturated air-dried, and K-saturated heated to 550ºC for 2 hours. X-ray diffraction technique, (XRD), was used to identify the unknown minerals using Melvern Panalytical Empryan (2020) device model, Netherlands. Cu-target tube and Ni filter at 40 kV and 30 mA. Identify the minerals constituting, according to PDF-2 cards release 2020, scintillation counter, A total of (44) representative samples (30 from the soil samples and 14 from the fertilizers) were analyzed radiometrically. This was carried out using the high efficiency γ- ray spectrometer (NaI"Tl"-Detector). The main radioelements: U, Th, Ra, and K are determined through four energy regions of interest (ROIs). Since U and Th are not γ-emitters, they are measured indirectly using their most common γ- ray emitting radionuclides, Th-234 and Pb-212 respectively. Ra is determined through the effective γ- line of Pb-214 while K is determined directly through the line of K-40 [25].

3 Results

3.1 Radionuclides distribution in the studied soils

For investigation of the studied soil samples collected from various governorates and the used fertilizers, these samples were radiometrically measured for their radionuclides content determination. These samples include ten samples from El Fayoum governorate, ten from El Sharqia governorate, and ten samples from El Giza governorate, as well as the used phosphatic fertilizers [ten samples from phosphogypsum and ten samples from superphosphate (SSP)].

The distribution of different radioelements in soil and fertilizers will be discussed in the following paragraphs. The average of radionuclide contents in El Fayoum governorate varies between 0.34 and 1.00 ppm with an average of 0.66 for eU, between 3 and 6 ppm with 4.83 as an average for eTh, between 1.00 and 4.00 ppm with mean 2.50 for radium equivalent uranium (RaeU) and between 0.78% and 1.81% with average 1.28 for potassium.

For El Sharqia governorate, eU ranges from 1 to 1.9 ppm and averages 1.3, eTh falls in the range from 5.00 to 7.92 ppm with a mean of 5.9, RaeU has a range from 2 to 5 ppm with an average of 3.5 while potassium content alters from 1.2 to 2.3% with a mean value 1.7.

Concerning El Giza governorate, eU modified from 0.29 to 2.00 ppm and averaged 1.03, eTh from 3 to 6.3 ppm with a mean value of 4.83, RaeU from 1.00 to 4.00 ppm an average of 2.58, and K from 0.84 to 1.55% and averaging 1.25%.

Notably, the concentration of radionuclides in various governorates is lower than the permissible levels recorded in [26]; [27]; [28]; [29]; [30]; [31]; [32]; [33], suggesting the un hazard limits of radionuclide contents. The Th/U ratio of the studied soils exhibits values ranging between 1.49 and 5.47, which reflect the poor weathering and rapid deposition of rock detritus [34]; [35]; [36]; [37]; [32].

3.2 Mineralogical investigation of the soil samples

It is worth mentioning that a higher concentration of radioelements was found in the El Sharqia governate relative to the others. This could be the presence of clay minerals montmorillonite-chlorite and kaolinite with gypsum and minerals such as rutile and quartz as indicated by X-ray diffraction analyses for El Sharqia soil (Figs. 2 & 3). An increase in the proportion of thorium concentration for El Sharqia soil may be correlated with the presence of rutile and quartz that probably originated from the black sand source.

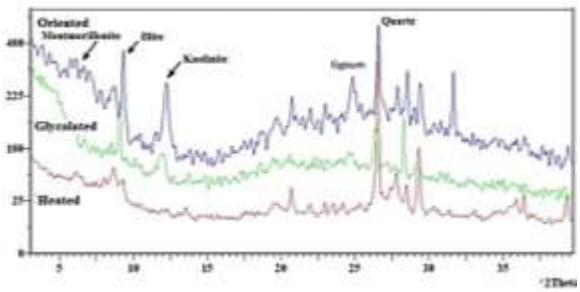

Fig.2. X-ray diffraction pattern of clay minerals in El Sharqia Governorate soil.

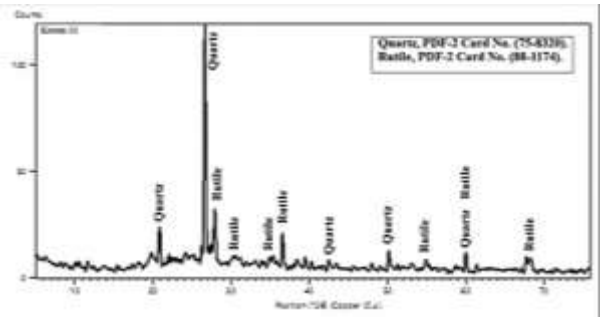

Fig.3. X-ray diffraction pattern of rutile mineral in El Sharqia Governorate soil.

An increase of radioelements contents in El Giza soil may be revised to its adsorption on clay mineral montmorillonite-chlorite, Kaolinite, and illite-muscovite minerals [38]; [39], (Figs. 4).

Fayoum soil samples are characterized by the presence of clay minerals (Kaolinite, Chlorite-vermiculite-montmorillonite, illite) with zirconium silicate minerals (Figs. 5 & 6).

The presence of hydroxylapatite minerals in El Sharqia soils may be related to their slightly higher contents. Hydroxyapatite has a strong affinity for certain metals, including radioelements (Figs. 7).

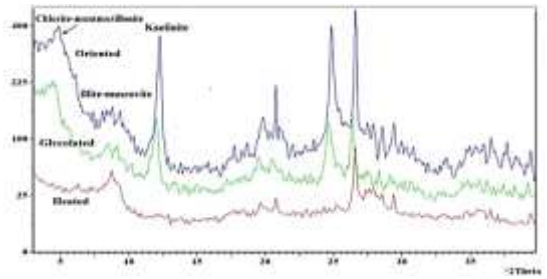

Fig.4. X-ray diffraction pattern of clay minerals in El Giza soil.

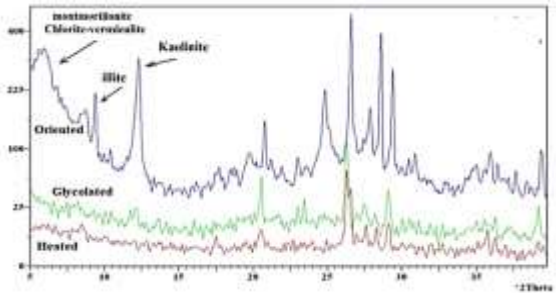

Fig.5. X-ray diffraction pattern of clay minerals in El Fayoum soil.

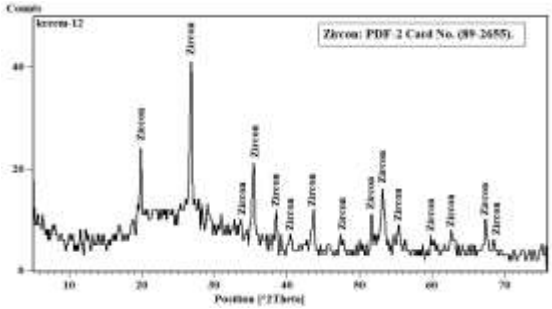

Figure 6. X-ray diffraction pattern of Zirconium Silicate mineral, El Fayoum soil.

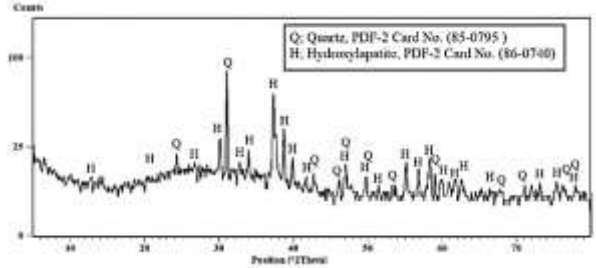

Fig.7. X-ray diffraction pattern of hydroxylapatite minerals identified in El Sharqia soil.

3.3 Inter-element relations of radionuclides

The interelement relations of radioelements clarify the fractionation of radionuclides in the studied soils due to differences in mobilization during various conditions invalid in soil formation. Uranium-thorium intercept exhibits nearly no or weak correlation between these elements, where correlation coefficient in different soils are (in El Sharqia, R^2=0.063, El Giza, R^2=0.0.405 and El Fayoum, R^2=0.121), indicating uranium mobilization by water of irrigation out of thorium (Fig. 8a). eTh-eU-eTh relation shows a weak or moderate positive correlation, in contrast to the relationship between eU and eTh-eU that indicates no or moderate negative correlation confirming the previous result (Figs. 8b & c). Potassium does not correlate with both eU and eTh, showing that these elements weren't affected by alteration processes (Figs. 8d & e).

From the determination of both the equivalent Uranium (eU) and Radium (RaeU) concentrations (in ppm) radiometrically, the equilibrium factor (P) could be calculated as P = eU /Ra eU [35]; [40], [32]; [14]) . In the equilibrium case, the activity ratio between the parent/daughter or between daughter/daughter is equal to unity, the values deviate from unity indicating disequilibrium conditions.

In the studied soil samples, the equilibrium factor (P) average is 0.33, 0.41 and 0.44 for El Fayoum, Sharqia and El Giza soils, which is lower than Unity, suggesting the presence of negative disequilibrium due to uranium migration concerning radium in the studied soils (Fig. 8f and Table 1).

Table 1. Radioelement contents (ppm and Bq/kg) of the studied farm soils and their ratios.

Ser. No.	Sample No.	eU (ppm)	eTh (ppm)	RaeU (ppm)	K%	Th/U	U/RaeU	Th/K	eU-eTh/3.5
El Fayoum Governorate									
1	F1	1	6	4	1.43	5.4	0.25	4.20	-0.71
2	F2	0.55	4	3	1.08	6.54	0.18	3.70	-0.59
3	F3	0.89	4	2	1.33	4.49	0.45	3.01	-0.25
4	F4	0.66	5	1	1.23	6.82	0.66	4.07	-0.77
5	F5	0.49	3	3	1.02	6.12	0.16	2.94	-0.37
6	F6	0.83	6	2	1.23	5.51	0.42	4.88	-0.88
7	F7	0.57	6	3	1.81	9.47	0.19	3.31	-1.14
8	F8	0.77	4	2	1.27	5.19	0.39	3.15	-0.37
9	F9	0.339	6	3	1.63	15.93	0.11	3.68	-1.38
10	F10	0.44	5	2	0.78	10.22	0.22	5.77	-0.99
min		0.34	3.00	1.00	0.78	4.49	0.11	2.94	-1.38
max		1.00	6.00	4.00	1.81	15.93	0.66	5.77	-0.25
aver		0.66	4.83	2.50	1.28	7.99	0.32	4.06	-0.76

Ser No.	Sample No.	eU (ppm)	eTh (ppm)	RaeU (ppm)	K%	Th/U	U/RaeU	Th/K	eU-eTh/3.5
El Sharqia Governorate									
1	Sh1	1	6.3	3	1.5	6.33	0.33	4.67	-1.00
2	Sh2	1.5	5.4	2	1.22	4.00	0.75	4.92	-0.21
3	Sh3	1.66	5.4	4	1.34	3.61	0.42	4.48	-0.05
4	Sh4	1.89	6.3	5	2.14	3.70	0.38	3.27	-0.11
5	Sh5	1.1	5.4	4	1.83	5.45	0.28	3.28	-0.61
6	Sh6	1.33	5.4	3	1.34	4.51	0.44	4.48	-0.38
7	Sh7	1.12	5	4	1.88	4.46	0.28	2.66	-0.31
8	Sh8	1	7.92	3	2.27	7.21	0.33	3.52	-1.29
9	Sh9	1.11	6.3	5	1.88	6.31	0.22	3.72	-0.89
10	Sh10	1.05	7.92	2	1.49	7.62	0.53	5.37	-1.24
	min	1.0	5.0	2.0	1.2	3.61	0.22	2.66	-1.29
	max	1.9	7.92	5.0	2.3	7.20	0.75	5.37	-0.05
	Avg.	1.3	5.94	3.5	1.7	5.52	0.41	4.03	-0.62
El Giza Governorate									
1	GS1	1	4	3	1.31	4.00	0.33	3.05	-0.14
2	Gs2	1	6	2	1.02	6.00	0.50	5.88	-0.71
3	Gs3	0.68	4	2	0.85	5.88	0.34	4.71	-0.46
4	Gs4	1	3	3	1.31	3.00	0.33	2.29	0.14
5	Gs5	0.57	6.3	4	1.53	11.05	0.14	4.58	-1.43
6	Gs6	0.8	5	3	1.53	6.25	0.27	3.27	-0.63
7	GS7	2	4	2	1.5	2.00	1.00	2.67	0.86
8	Gs8	2	3	3	0.84	1.50	0.67	3.57	1.14
9	Gs9	0.29	5.4	1	1	18.53	0.29	6.00	-1.42
10	Gs10	0.67	6	3	1.55	8.96	0.22	3.87	-1.04
	min	0.29	3.00	1.00	0.84	1.50	0.14	2.29	-1.43
	max	2.00	6.3	4.00	1.55	18.53	1.00	6.00	1.14
	Avg.	1.03	4.83	2.58	1.24	7.73	0.44	4.01	-0.33

3.4 Radionuclides distribution in the superphosphate and phosphogypsum

The ore phosphate mixture will be treated with sulfuric acid, which ends with phosphoric acid (PA) and phosphogypsum (PG). Chemical treatment of a mixture of ore with phosphoric acid will end with the products, single superphosphate (SSP) and triple superphosphate (TSP). This was shown in the following chemical reactions:

$$Ca_{10}(PO_4)_6F_2 + 10\,H_2SO_4 + 20\,H_2O \rightarrow 10\,CaSO_4.2H_2O + 6\,H_3PO_4 + 2\,HF \quad (1)$$

$$0.7\,Ca_{10}(PO_4)_6F_2 + 7\,H_2SO_4 + 3.5\,H_2O \rightarrow 4.2\,H_3PO_4 + 7\,CaSO_4.\tfrac{1}{2}H_2O + 1.4\,HF \quad (2)$$

$$0.3\,Ca_{10}(PO_4)_6F_2 + 4.2\,H_3PO_4 + 3\,H_2O \rightarrow 3\,Ca(H_2PO_4)_2.H_2O + 0.6\,HF \quad (3)$$

Generally, the specific activities of natural 238U series radionuclides in phosphate fertilizers depend on their levels in the used raw phosphate ore material. Radioactivity levels in phosphate ores vary according to their origin (sedimentary, volcanic, or biological origin), where 238U and its decay products tend to be elevated in phosphate deposits of sedimentary origin due to the accumulation of dissolved uranium, in the form of uranyl complex, in the seawater during the geological formation of the phosphate rocks [13]; [23]. A typical concentration of 238U in sedimentary phosphate deposit is 1500 Bq/kg [20]; [21]. [41] observed that the high uranium concentration in triple superphosphate, about the simple superphosphate, depends on the mode of production. For the investigated fertilizer samples, they have radionuclides content in comparison with the soil samples as will be shown.

The uranium concentration in the superphosphate variates from 21 to 28 ppm with 21.49 as an average, thorium from 1.22 to 1.55 ppm and averaging 1.21, radium equivalent uranium from 29 to 35 ppm with an average of 32.3, while potassium percentage from 0.40 to 1.43% with average 0.81. The activity concentrations of uranium and radium in all superphosphate samples were higher than the worldwide average of 32 and 33 Bq/kg, respectively [26].

The activity concentrations of thorium in all samples were less than the worldwide average of 45 Bq/kg. On the other hand, the activity concentrations of K-40 in the superphosphate samples were less than the worldwide average of 412 Bq/kg [26] Phosphogypsum samples have uranium and thorium contents less than the superphosphate fertilizer but with higher radium and potassium contents. Equivalent uranium contents vary between 28 and 33.00 ppm with 30.21 as an average, thorium between 3 and 6 ppm and averaging 3.11, radium equivalent uranium between 26 and 31 ppm with an average of 26.30, where potassium between 0.43 and 1.33% with an average 0.50%. It is notable the presence of high radium concentration in phosphogypsum, which could be related to its precipitation with calcium and Ba as Ra sulfates.

The activity concentrations of uranium and radium in various phosphogypsum samples were higher than the worldwide average of 33 and 32 Bq/kg, respectively [26], while thorium in all samples was lesser. The activity concentrations of K-40 in most phosphogypsum samples were less than the worldwide average [26].

The eTh/eU average of both superphosphate and phosphogypsum are 0.13 and 0.05 fertilizers [42];[43], [44]; [45]. The radioelement enrichment in these fertilizers is mainly related to the presence of fluorapatite and carbonate hydroxylapatite associated with gypsum mineral (Figs. 9,13), and associated minerals Corundum (Aluminum Oxide), Augelite (Aluminum Phosphate Hydroxide) in superphosphate (Fig. 12), Additionally, the presence of the following minerals, phosphogypsum contained associated minerals Augelite (Aluminum Phosphate Hydroxide), Carbonate-hydroxylapatite (Calcium Carbonate Phosphate Fluoride Hydroxide) and Gypsum (Calcium Sulfate Hydrate), (Fig. 13).

3.5 Mineralogical investigation of the superphosphate and phosphogypsum

The mineralogical studies of phosphogypsum and superphosphate samples using the X-ray diffraction technique revealed the identification of gypsum (Calcium Sulfate Hydrate), fluorapatite (Calcium Phosphate Fluoride) (Fig. 9), anhydrite (Calcium Sulfate) (Fig. 10), berlinite (aluminum phosphate) (Fig.11), Augelite (Aluminum Phosphate Hydroxide) and corundum (Fig. 12), carbonate hydroxylapatite (Calcium Carbonate Phosphate Fluoride Hydroxide) minerals (Fig . 13).

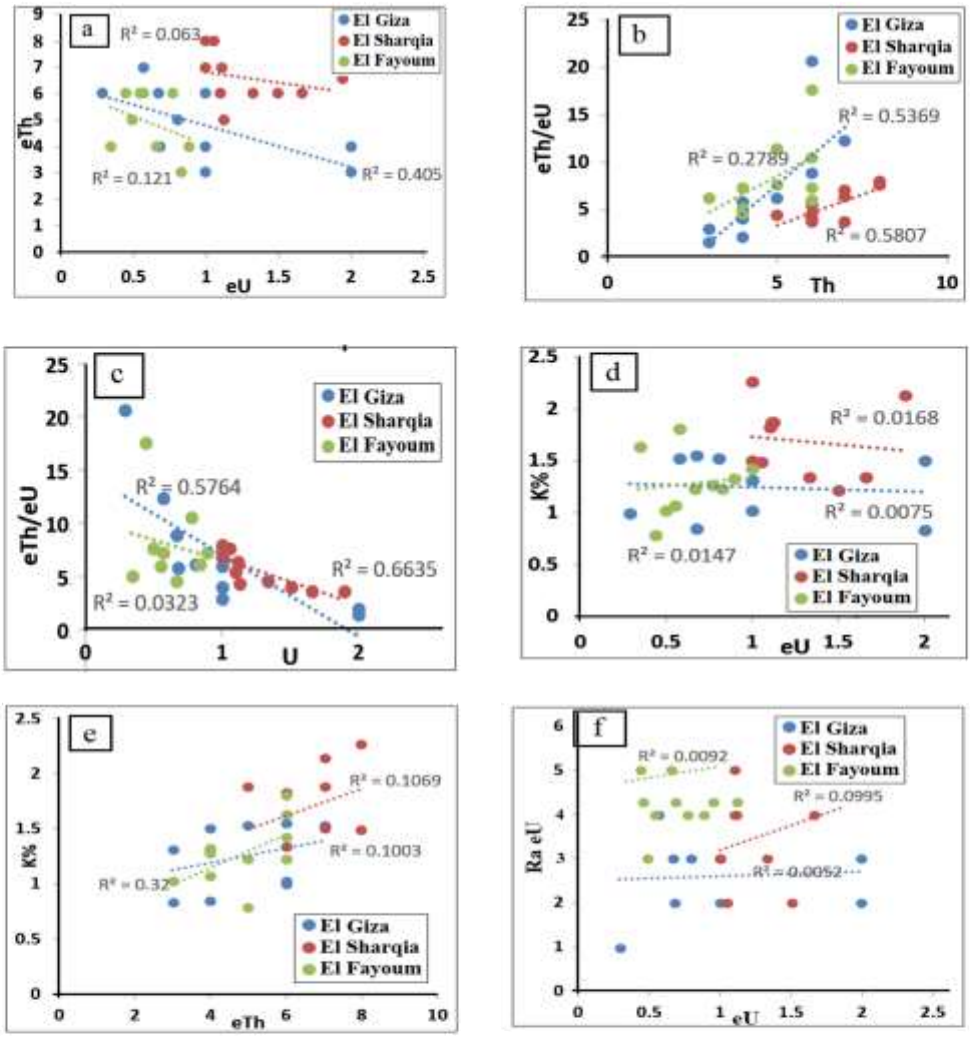

Fig. 8. (a) eU-eTh, (b) eTh-eTh/eU, (c) eU-eTh/eU, (d) eTh-K, (e) eU-K, (f) eU-Ra eU of the studied farm soils.

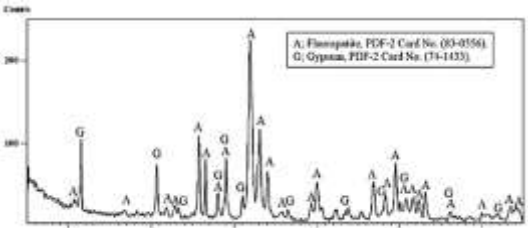

Fig.9. X-ray diffraction pattern of fluorapatite associated with gypsum in superphosphate.

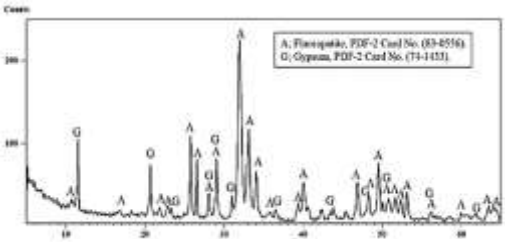

Fig.10. X-ray diffraction pattern of minerals identified in phosphogypsum samples.

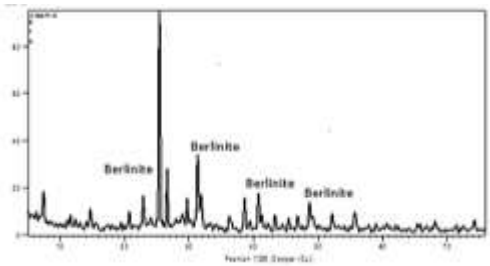

Fig. 11. X-ray diffraction pattern of berlinite associated with Gypsum mineral identified in superphosphate.

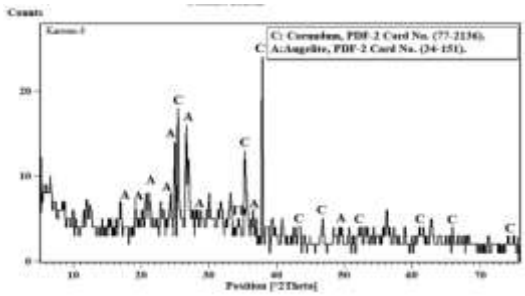

Fig.12. X-ray diffraction pattern of corundum and associated minerals identified in superphosphate and phosphogypsum.

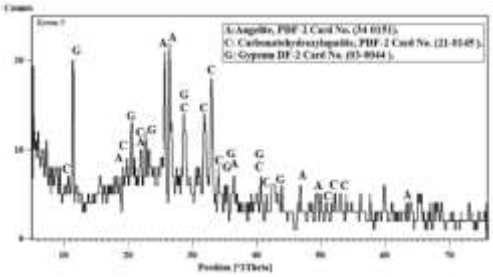

Fig. 13. X-ray diffraction pattern of Augelite and associated minerals identified in superphosphate and phosphogypsum.

3.6 Inter-element relations in fertilizer

In superphosphate, the uranium-thorium cross plot shows a moderate positive correlation, manifesting the mobility of the two elements away from each other (Fig. 14a). Ill-defined correlation between eTh with eTh/eU ratio, in contrast to moderate negative correlation (R^2=0.488) of eU with eTh/eU ratio confirms the previous result (Figs. 14b & c). eTh-K intercept illustrates a weak positive correlation, suggesting little amount of thorium adsorption on clay minerals, contrasting eU shows a moderate negative correlation, indicating U migration with alteration processes (Figs. 14d & e).

In phosphogypsum, eU illustrates little, if any, relationship to thorium, suggesting differential mobility of these elements in oxidation conditions (Fig. 15a). eU and eTh cross plot with eTh/eU clarify the decreasing of uranium with increasing thorium and the opposite (Figs. 15b & c). Uranium and thorium crosscut with potassium show migration out of both elements with feldspar alteration to clay minerals (Figs. 15d & e).

Factor in superphosphate samples ranges between 0.9 and 1.21 with 1.09 as an average, manifesting positive equilibrium condition as reported by [14], resulting from uranium migration during phosphate rock processing. On the contrary, phosphogypsum samples have negative equilibrium (from 0.51 to 0.78 with an average of 0.67), due to uranium migration out and radium precipitation as radium sulfate (Figs. 14f, 15f & table 2).

Table 2. Radioelement contents (ppm and Bq/kg) of the studied superphosphates and phosphogypsum with their ratios.

Ser No.	Sample No.	eU (ppm)	eTh (ppm)	RaeU (ppm)	K%	Th/U	U/RaeU	Th/K	eU-eTh/3.5
Superphosphates									
1	C1	28.8	1.33	38	0.55	0.04	0.74	2.42	28.15
2	C2	25	1.45	34	0.77	0.06	0.69	1.51	24.59
3	C3	22	1.22	34	0.72	0.06	0.55	1.69	21.65
4	C4	28.8	1.55	36.9	0.4	0.05	0.78	3.88	28.40
5	C5	25.2	1.24	37	1.41	0.04	0.76	0.88	27.65
6	C6	22	1.38	34	1.33	0.06	0.51	1.04	21.61
7	C7	21	1.29	20	1.43	0.06	0.72	0.90	20.63
min		21.00	1.22	29.00	0.40	0.04	0.51	0.88	20.63
max		28.8	1.55	35.00	1.43	0.06	0.78	3.88	28.15
aver		21.49	1.21	32.3	0.81	0.05	0.67	1.90	25.73
Phosphogypsum									
1	S1	31	4	30	0.99	0.13	1.03	4.04	29.86
2	S2	28	5	31	1.33	0.18	0.90	3.50	26.57
3	S3	30	6	28	1.12	0.20	1.07	5.36	28.29
4	S4	32	3	29	0.48	0.09	1.21	6.25	30.72
5	S5	31	3	26	0.46	0.10	1.19	6.52	27.12
6	S6	30	3	29	0.63	0.09	1.17	4.76	29.82
7	S7	32	4	29	0.43	0.13	1.10	9.30	27.77
min		28.00	3.00	26.00	0.43	0.09	0.90	3.50	26.57
max		33.00	6.00	31.00	1.33	0.20	1.21	9.30	30.72
aver		30.21	3.11	26.30	0.50	0.13	1.09	5.84	27.36

4 Conclusions

The studies were conducted on selected cases of agricultural soil in addition to two types of agricultural fertilizers. The study covered the regions of Zahr Sharab, Hawarat El Maqata, and El Suf. Which belong to El Sharqia, Fayoum, and Giza governorate, respectively, and samples of superphosphate and phosphogypsum fertilizers.

Mineralogical studies of soils show the presence of clay minerals montmorillonite-chlorite, Kaolinite, illite-muscovite, chlorite-vermiculite-montmorillonite with the presence of hydroxyapatite, with rutile and zirconium silicate mineral. In addition to gypsum (Calcium Sulfate Hydrate), anhydrite (Calcium Sulfate), Augelite (Aluminum Phosphate Hydroxide), and Carbonate-hydroxylapatite (Calcium Carbonate Phosphate Fluoride Hydroxide) were identified in fertilizer samples. The

average of radionuclide contents in soil samples shows eU (0.66, 1.3, 1.03 ppm), eTh (4.83, 5.94, 4.83 ppm), K (1.28, 1.7, 1.24 %), and RaeU (2.5, 3.5, 2.58 ppm) recorded in Fayoum, El Sharqia, and Giza governorate respectively. And eU (21.49, 30.21 ppm), eTh (1.21, 3.11 ppm), K (0.81,0.50 %), and RaeU (32.3, 26.30 ppm) recorded in superphosphate and phosphogypsum fertilizers. Notably, the concentration of radionuclides in various governorates is lower than the permissible levels recorded in worldwide limits. Uranium and thorium contents in soil samples are revised to their adsorption on clay mineral montmorillonite and kaolinite, in addition to the presence of hydroxylapatite with the presence of rutile and quartz that probably originated from old black sand source in El Sharqia soil. Equilibrium conditions in various governorates indicate disequilibrium processes due to uranium migration, maybe by the water of irrigation. The investigated fertilizer samples, have higher radionuclides content in comparison with the soil samples. The presence of fluorapatite and carbonate hydroxylapatite might be the main reason for significantly high values. The notable recorded radium concentration in phosphogypsum could be related to its precipitation with calcium and Ba as Ra sulfates.

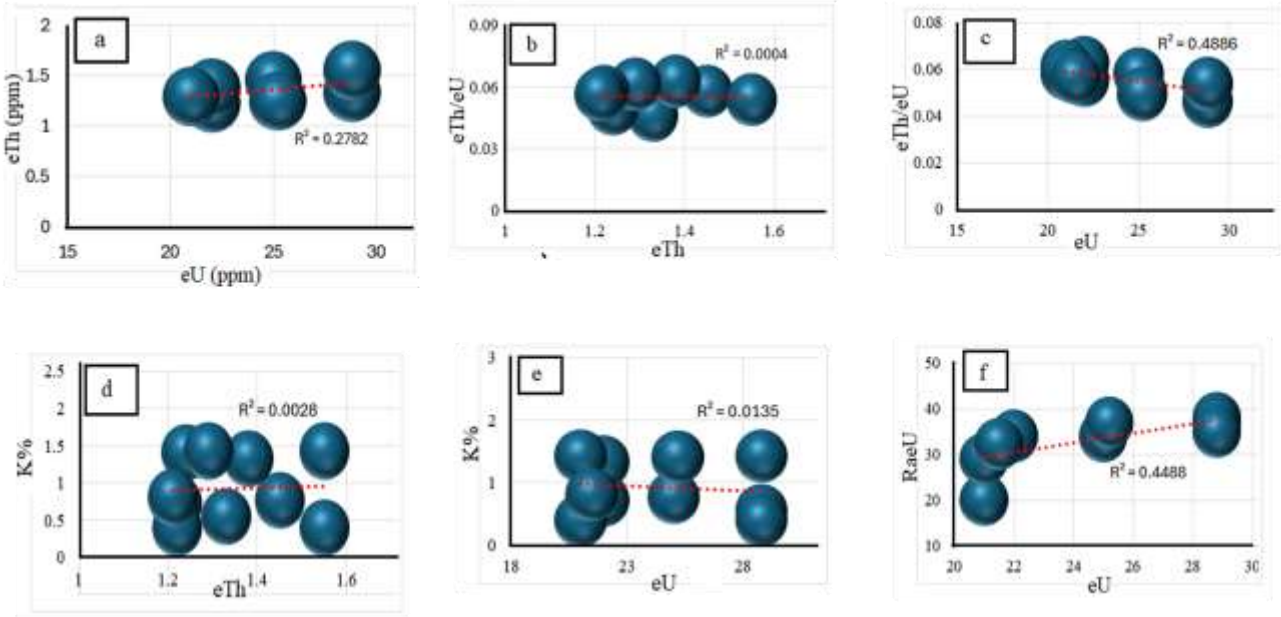

Fig. 14. (a) eU-eTh, (b) eTh-eTh/eU, (c) eU-eTh/eU, (d) eTh-K, (e) eU-K, (f) eU-Ra eU of the studied superphosphate fertilizer.

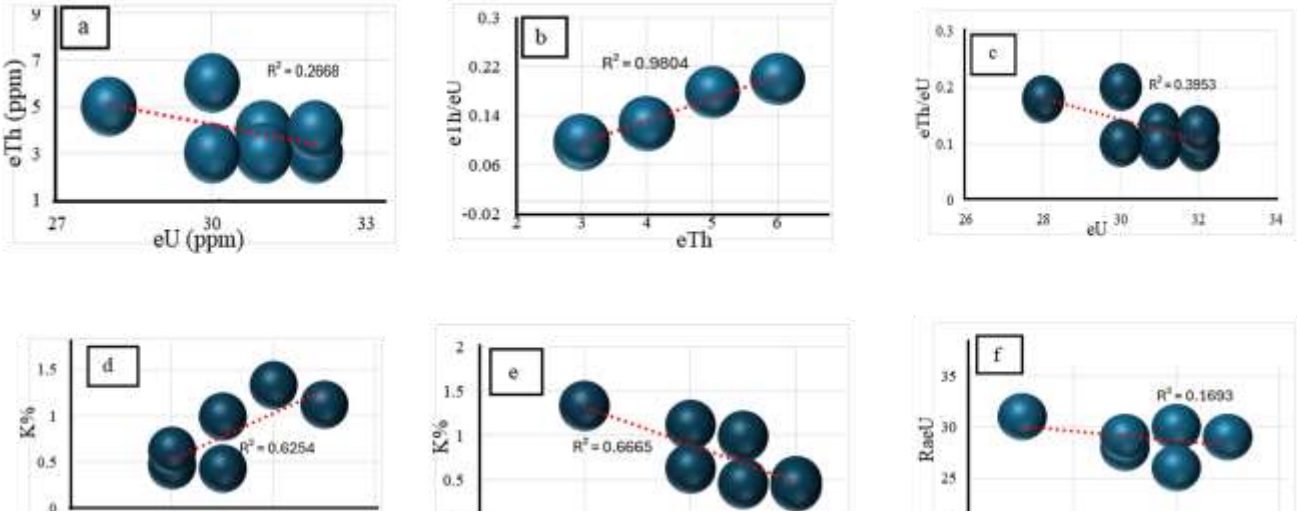

Fig.15. a) (eU)/eTh, b) (eTh)/(eTh/eU), c) (eU)/(eTh/eU), d) (eTh)/(K), e) (eU)/(K), f) (eU)/(Ra eU) of the studied phosphogypsum fertilizers.

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