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RARE EARTH ELEMENTS IN NILE SEDIMENTS AT LUXOR AND ASWAN DISTRICTS: GEOCHEMISTRY, ENRICHMENT AND ENVIRONMENTAL IMPACT

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Abstract

The expansion in the use of rare earth elements (REEs) in last decades has led to the emergence of the problem of soil pollution with these elements and their ecological risk. This research aims to assess soil pollution with REEs in Aswan and Luxor districts, Egypt, and their ecological risk. Agricultural soil samples were collected and prepared for mineralogical and chemical investigation. Pollution indices were applied to investigate the degree and hazard of the occurrence of these elements in the study areas. Mineralogically, the studied soils composed of montmorillonite and kaolinite as clay minerals as well as quartz and calcian-albite. The recorded average ΣREEs concentration was 160.8 and 248.3 µg/g for Aswan and Luxor; respectively. Both regions have the same trend, Ce is the highest recorded element and Pr is the lowest. The REEs are most probably derived from the phosphate fertilizers and/or Phosphate Mining in El Sebayia. In addition, Sc and Sm are weakly correlated with Al and Fe which indicated that the clay minerals can be play a significant role in their mobilization, as well as iron has the capability of scavenge them in the studied soils in Luxor and Aswan governorates. The contamination factor indicated the low contamination with La and Nd, moderate contamination with Ce, Pr, Sc and Y, as well as considerable contamination with Sm. Gurna and Habo soils (Luxor Governorate) recorded high concentration of REEs than which in Aswan Governorate. REEs haven't ecological risk in the study areas. Finally, a detailed baseline study about the distribution of potential toxic elements in the Egyptian environmental constituents (soil, water, air and plant) must be done.

Keywords: Rare Earth Elements; Pollution Indices; Soil Mineralogy; Anthropogenic; Egypt.

1. Introduction

Egypt is one of the worldwide poor countries in terms of agricultural land, as the percentage of agricultural land in Egypt represents about 3.7%, concentrated around the banks of the River Nile and in the Delta, and the rest of Egypt's area is desert land. Despite the expansion of reclamation of desert lands, the per capita share in Egypt decreased from 0.12 hectares in 1950 to 0.04 hectares in 2013 due to the population increase [1-3]. Soil is one of the most important ecological compartment that supports human life by providing humans, animals and plants with food and other necessities such as building materials. Soil also supports the regulation and purification of water supplies. However, human activities and technological progress have recently caused many adverse impact on the soil. The pollution of soil with chemicals become one of the worldwide problems owing to its impact on food security and human life [4-6]. Many Authors [e.g. 7,4,8] pointed out the pollution of agricultural soil in Egypt with heavy metals.

The term "Rare earth elements (REEs)" is used to refer to the lanthanides series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in addition to Sc and Y. The average concentration of REEs in the earth's crust reaches 130 – 240 µg/g, which is considered one of the highest concentrations of exploited elements, as well as much higher than their concentration in chondrites [9].

In nature, REEs don't exist as individual native metals; Eu, Co and Ag resulting of their reactivity. But, they are present associated with several ores as accessory minerals. They are nearby in occurred in a wide variety of minerals such as phosphates, carbonates, silicates and oxides found in a few geological environments. The most important economic sources of REEs are monazite, bastnaesite, loparite and the lateritic clays [10]. In addition, REEs occurs in more than 250 minerals as crucial constituents in their chemical formula and crystal structure [11,12]. Presently, these metals are very critical to numerous contemporary technologies such as cell phones, televisions, LED light bulbs and wind turbines [13]. As well as, they have significant applications in agriculture, medicine together with the environmental effects. Resulting of the magnetic, optical, catalytic and electronic properties, REEs raise the recompense of a variety of technologies; lower energy consumption, velocity, elevated effectiveness, and thermal strength [10,14]; hence, REEs can be considered as industrial vitamins [10, 15].

Recently, due to the ability of rare earth elements to enter the food chain and persist in the environment, the appearance of rare earth elements in soil has become a matter of concern [16,17]. Wiche and Heilmeier [18] reported that REEs can

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be adsorbed by both herbs and grasses. It has been pointed out that the presence of these elements in soil can cause serious consequences for ecosystems, agricultural productivity, water resources and human health [19, 17]. The main source of REEs accumulation in is the use of phosphatic fertilizers [20]. In soils, REEs originate mainly from the parent material [21, 22]. Industrial and agricultural (Fertilizers) activities can release REEs into water resources and soil, and their hazardous accumulations [23].

For assessment of soil contamination, many pollution indices have been proposed in the last decades; i.e. contamination factor, index of geoaccumulation and enrichment factor, and of ecological impacts the ecological risk indices are applied [24, 25, 8]. The aim of this study was to evaluate and assessment the concentrations of rare earth elements in agriculture soil in Aswan and Luxor districts through Appling pollution indices.

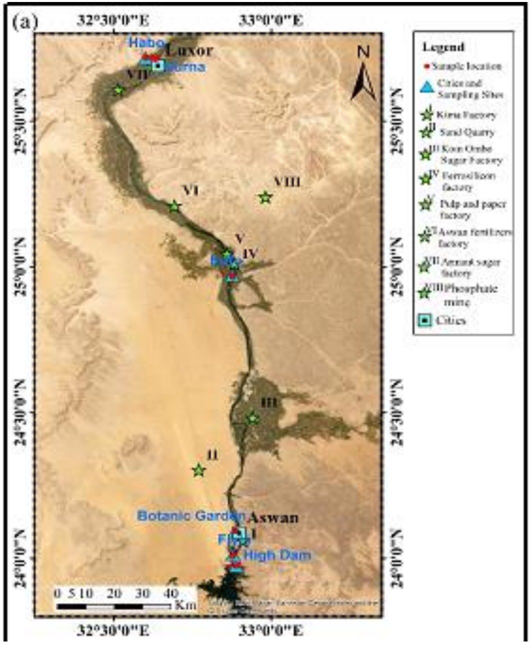
2. Materials and Methods

2.1. Study area

The study area represents the southern part of the Nile Valley and includes the governorates of Aswan and Luxor. The study area is characterized by international fame and intense tourism activity due to the concentration of Pharaonic monuments there. The study area also contains many existing industries such as chemicals, fertilizers, paper, and many mines and quarries such as iron, phosphate, and building materials (Fig. 1).

The River Nile had impacted regionally and locally by pollution as a result of adverse human activity. Lake Victoria is biologically polluted [26], Lake Tana [27] and the Nile at Sudan and Egypt [28,29] are bacteriologically and chemically polluted.

Regionally, the geology of the River Nile basin is governed by rocks and tectonics from the Precambrian to the Phanerozoic Locally, several authors attempted to explain the origin of the River Nile such as Butzer and Hansen [30], Said [31,32], Issawi and McCauley [33], Omer [34] and Abdel-Haleem et al. [35].



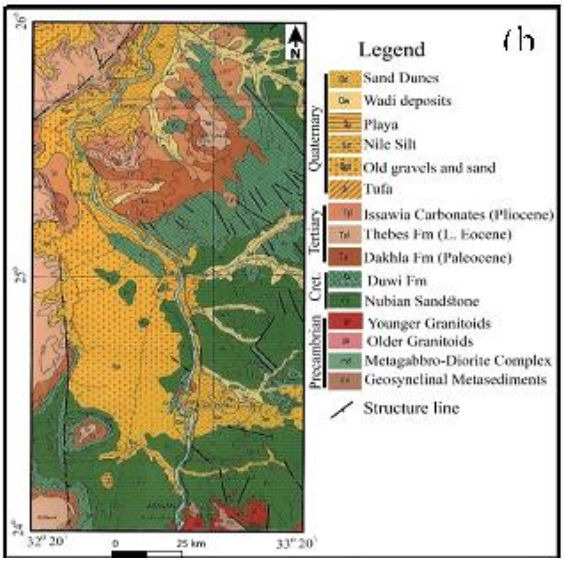


Fig. 1: (a) Location map of the sampling sites, (b) Geologic map of the study area (After [37]).

Geologically, the study area contains rocks from the Precambrian to the Quaternary (Fig. 2). The Nile floodplain represents the cultivated lands located in the east and west of the River Nile. They are composed of clays and silts with sandstone intercalations. These sediments are extending on both sides of the Nile stream. The main source of this alluvial soil is the mafic/ultramafic rocks in the Ethiopian hinterlands and Red Sea Mountains [31, 34].

2.3. Sampling and analyses

To represent the eastern and western sides of the Nile, seventeen cultivated soil samples were collected from six sites: Gurna and Habo in Luxor, and Edfo, Fila, High Dam, and Botanic Garden in Aswan (Fig. 1). At each sampling station, the surface soil sample (top 15 cm) was collected using shovel from four different sites over an area nearly 30 m^2 and mixed together. About 1 kg of soil material was taken at each sampling station, sealed in clean labeled polyethylene bags and transported to the laboratories. In the laboratory, the soil samples were air dried at room temperature for one week, crushed softly and sieved with 2 mm screen for removing stones and plant remains. The obtained soil samples were coned, quartered and sub-samples (about50 g) were oven dried at 105 °C overnight. For analysis, each sample was homogenized and pulverized to pass through a 63-mesh sieve.

The microwave (closed system) was used for digestion of shale samples according to European Committee for standardization [35]. Briefly, a 0.5 g of homogenized soil sample was weighted and transferred in the PTFE vessels for microwave digestion. Subsequently, 9 ml of nitric acid (69%) and 1 ml H_2O_2 were added to the sample. The vessel was closed completely and excellently, then transferred to the microwave until complete of digestion. Digestion was performed in the microwave oven by temperature-controlled program: heating to 200 °C for 15 min, holding time 15 min, cooling to 85 °C for 15 min. After cooling to room temperature the content of the vessel was transferred to a volumetric flask (25 mL) and diluted with ultrapure water to the mark, then ready for analysis by ICP-OES at National research Centre. The mineralogical composition was studied by the X-Ray Diffraction (XRD) analyses ((Philips type ’PanALytica’ equipment model ’X-Pert-PRO’ with ’Ni-filter), a Cu-radiation (λ=1.542 Å) of 45 kV, 35 mA, and a normal scanning speed of 0.03°/sec, the diffractograms were obtained using a range of 2° to 60°) at the Egyptian Mineral Resources Authority (Dokki, Egypt).

3. Results and Discussion

3.1. Mineralogy

The XRD analysis showed three mineral phases (quartz, clays and albite) in the studied soils. Quartz represented the main component, clay minerals are composed of montmorillonite and kaolinite, in addition to calcian-albite. In suitable media of excess Na may be mixed with Ca and produced calcian- albite as Ca-Na-Al silicate. X-ray diffraction appears the samples of Gurna composed of (40%) quartz, (26%) montmorillonite, (14%) kaolinite and (20%) calcian albite. Habo samples are consists of three phases; montmorillonite (44%), kaolinite and (18%) and quartz (38%), also, Edfo samples show three phases; montmorillonite (33%), calcian-albite (15%) and quartz (52%) (Fig. 2).

The XRD analysis showed the high percentage of quartz (75%) in the samples of the High Dam, calcian-albite (10%) and (15%) magnesian-calcite. Fiyla soils consist of (50%) quartz, (25%) montmorillonite, (10%) kaolinte and (15%) calcian-albite. Finally, the Botanic Garden samples are distinguished by high content of quartz (70%) and low of kaolinte (3%), as well as, (10%) montmorillonite and, (7%) calcian-albite (Fig. 3). The findings of this study are in agreement with Bekir [38], Melegy and El-Agami [39] Salman [40] and Abou El-Anwar et al. [41], which ponted out the prevailing of quartz and some feldspars as non-clay minerals identified in the bulk soil samples as well as montmorillonite and kaolinite as clay minerals.

3.2. Geochemical Evaluation

The results of chemical analysis of REEs and, some major elements of the studied samples are quoted in Table (1). The interrelationship between them is given in Table (2).

3.2.1. Distribution of REEs

The studied soil samples composed mainly of Si, Al and Fe (Table 1) that reflect the mineralogical composition; silicate minerals (Figs. 2 and 3).

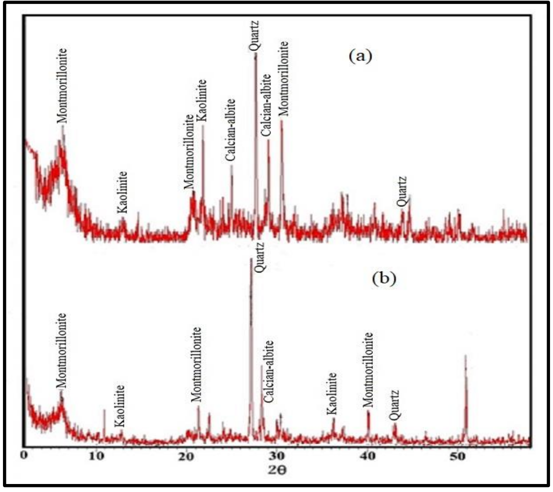


Fig. 2: X-ray diffraction patterns of the study agriculture soils from Luxor (a) Gurna and (b) Habo.

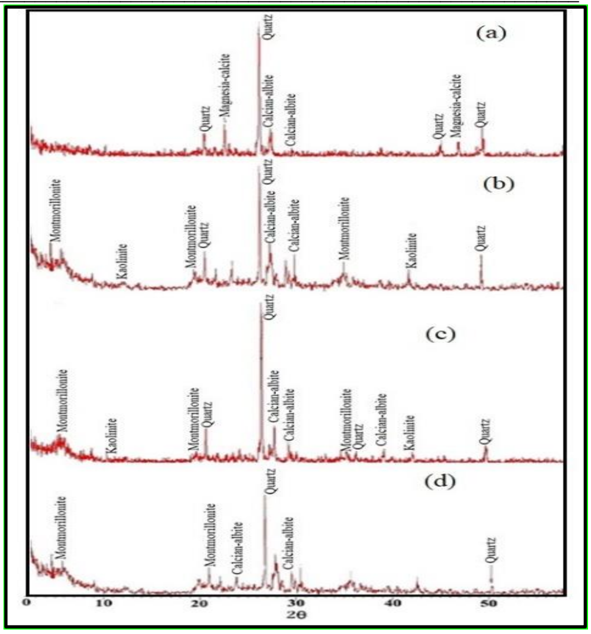


Fig. 3: X-ray diffraction patterns of the study agriculture soils from Aswan (a) High Dam, (b) Fiyla, (c) Botanic Garden and (d) Edfo.

The high Si/Al ratio in the studied samples indicates that the studied soil consists mainly of a mixture of quartz, montmorillonite and kaolinite [40, 42, 43] as appeared in the previous XRD results. The The average REEs were ranging from 120.2 to 255.7 µg/g in the studied agriculture soils (Table 1). Thus, this average of the total concentration of REEs in the studied agricultural soil (191.2 µg/g) is highly enrichment than those of Upper Continental Crust (UCC, 167.8 µg/g) and lower than those of the Post Archaean Australian Shale (PAAS, 209.08 µg/g), [44 and 45; respectively].

Sample No. (1) from Gurna samples recorded the highest content (302.9 µg/g) of REEs which corresponding to the highest Al, Fe and P contents (83047.2, 105749.3 and 12219.2 µg/g; respectively). Also, Gurna was has the highest value of ΣLREE (247.8 µg/g). In contrast, the lower REEs (112.5 µg/g) is in Botanic Garden area, (Sample No. 13). Y, La, Pr, and Sm values in the examined soil samples were comparatively greater than those of the world soil and variable with respect to the UCC and the PAAS (Fig. 4).

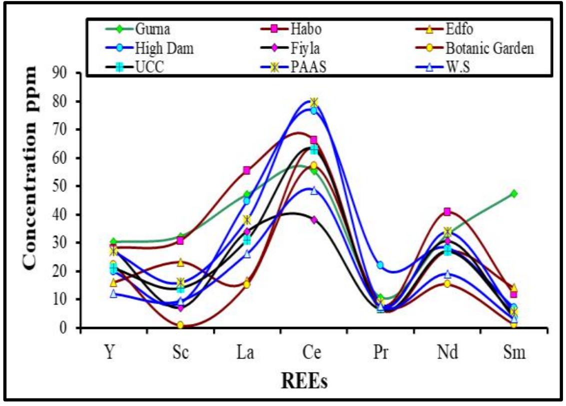


Fig. 4: Concentrations of the REEs in the studied localities as compared with those of UCC [45], PAAS [44] and world soil [50].

Table 1: Soil content of major and rare earth elements (µg/g).

Site		**S. No.**	Latitude “N”	Longitude “E”	Si	Al	Fe	P	Y	Sc	La	Ce	Pr	Nd	Sm	Si/Al	ΣREE	ΣLREE	ΣHREE	ΣLREE /ΣHREE	Ce /La	La /Sc
Luxor	**Gurna**	1	25.71661	32.63855	213882.2	83047.2	105749.3	12219.2	35.0	20.1	39.5	75.0	9.9	46.3	77.1	2.6	302.9	247.8	55.1	4.5	1.9	2.0
		2	25.71073	32.63281	234167.4	91304.3	104910	12044.6	27.5	33.4	45.8	40.1	10.4	18.6	5.0	2.6	180.8	119.9	60.9	2.0	0.9	1.4
		3	25.71455	32.62184	244169.8	86011.3	104140.7	13135.6	28.1	43.1	55.8	50.7	11.7	33.5	60.4	2.8	283.3	212.1	71.2	3.0	0.9	1.3
		mean			230739.8	86787.6	104933.3	12466.5	30.2	32.2	47.0	55.3	10.7	32.8	47.5	2.7	255.7	193.3	62.4	3.2	1.2	1.5
	Habo	4	25.71989	32.60257	204674.5	74154.9	81689.9	2138.4	28.5	22.9	50.9	71.5	8.4	47.6	7.8	2.8	237.6	186.2	51.4	3.6	1.4	2.2
		5	25.71647	32.60203	214256.2	67962.1	92880.3	2356.6	33.4	33.4	55.2	60.4	7.5	50.7	12.8	3.2	253.4	186.6	66.8	2.8	1.1	1.7
		6	25.71901	32.59942	206964.7	70238.1	87704.8	1352.8	22.5	35.9	60.1	66.7	7.8	23.8	14.8	2.9	231.6	173.2	58.4	3.0	1.1	1.7
		mean			208631.8	70785.1	87425	1949.3	28.1	30.7	55.4	66.2	7.9	40.7	11.8	2.9	240.9	182.0	58.9	3.1	1.2	1.8
Aswan	**Edfo**	7	24.96421	32.87734	211405	75478.2	85956.3	1483.8	14.7	25.8	14.9	67.0	6.5	31.7	12.7	2.8	173.3	132.8	40.5	3.3	4.5	0.6
		8	24.97	32.87778	239636	80824.1	101902.6	1789.2	17.5	20.8	18.4	60.1	6.9	22.4	15.7	3.0	161.8	123.5	38.3	3.2	3.3	0.9
		mean			225520.5	78151.2	93929.4	1636.5	16.1	23.3	16.7	63.6	6.7	27.1	14.2	2.9	167.6	128.2	39.4	3.3	3.9	0.7
	High	9	23.97124	32.86824	281748.7	66480.2	80640.8	3491.2	19.8	9.7	37.6	58.0	20.8	16.9	3.7	4.2	166.5	137.0	29.5	4.6	1.5	3.9
		10	23.97248	32.88913	284179.2	57534.9	41054.8	1352.8	22.7	7.8	46.2	91.7	18.1	35.7	8.0	4.9	230.2	199.7	30.5	6.6	2.0	5.9
		11	23.97746	32.89705	290489.1	59705.0	94069.3	1483.8	17.5	9.1	50.1	80.1	26.7	32.4	9.7	4.9	225.6	199.0	26.6	7.5	1.6	5.5
		mean			285472.3	61240.0	71921.6	2109.3	20.0	8.9	44.6	76.6	21.9	28.3	7.1	4.7	207.4	178.6	28.9	6.2	1.7	5.1
	Fiyla	12	24.01358	32.88129	261603.8	79818.4	97286.5	2705.7	26.8	9.8	37.9	57.3	7.8	23.6	0.9	3.3	164.1	127.5	36.6	3.5	1.5	3.9
		13	24.0119	32.87913	287778.2	47742.9	42873.2	654.6	28.6	6.4	28.3	13.0	6.8	32.9	5.3	6.0	121.3	86.3	35.0	2.5	0.5	4.4
		14	24.00582	32.87657	272213.8	68650.2	72527.8	1527.4	27.8	5.3	35.8	44.2	5.4	35.4	4.5	4.0	158.4	125.3	33.1	3.8	1.2	6.8
		mean			273865.2	65403.8	70895.9	1629.2	27.7	7.2	34.0	38.2	6.7	30.6	3.6	4.2	147.9	113.0	34.9	3.2	1.1	5.0
	Botanic	15	24.0952	32.88775	259734.2	78706.9	101063.3	1352.8	23.3	0.0	17.9	66.2	10.5	15.9	0.0	3.3	133.8	110.5	23.3	4.7	3.7	0.0
		16	24.0939	32.88687	237018.5	72725.8	87494.9	1527.4	21.0	0.0	15.1	50.2	9.5	17.5	1.0	3.3	114.3	93.3	21.0	4.4	3.3	0.0
		17	24.09218	32.88543	244310	80877.0	108197.2	1440.1	22.4	2.0	12.7	54.8	6.2	12.4	2.0	3.0	112.5	88.1	24.4	3.6	4.3	6.4
		mean			247020.9	77436.6	98918.5	1440.1	22.2	0.7	15.2	57.1	8.7	15.3	1.0	3.2	120.2	97.3	22.9	4.3	3.8	2.1
UCC					311381.9	81512.2	35249.8	654.6	21	14	31	63	7.1	27	4.7	3.8	167.8	132.8	35	3.8	2.0	2.2
PAAS					293527.2	100037.7	50496.7	698.2	27	16	38.2	79.6	8.83	33.9	5.55	2.9	209.08	166.08	43	3.9	2.1	2.4
W.S					252396.0	21172.0	24479.0	-	12	9.5	26.1	48.7	7.6	19	3.1	11.9	126	104.5	21.5	4.9	1.9	2.7

UCC: Upper Continental Crust (After [45])

PAAS: Post-Archean Australian Shale (After [44])

W.S: World soil (After [50])

Table 2: Correlation matrix for the studied elements

	Si	Al	Fe	P	Y	Sc	La	Ce	Pr	Nd	Sm	REE	LREE
Si	1.00												
Al	-0.55*	1.00											
Fe	-0.47*	0.84**	1.00										
P	-0.25	0.62**	0.45*	1.00									
Y	-0.23	0.12	0.02	0.48*	1.00								
Sc	-0.62**	0.39	0.31	0.56**	0.26	1.00							
La	-0.11	-0.10	-0.08	0.35	0.45*	0.62**	1.00						
Ce	-0.17	0.05	0.12	-0.08	-0.23	0.04	0.23	1.00					
Pr	0.55*	-0.34	-0.13	0.04	-0.32	-0.16	0.32	0.46*	1.00				
Nd	-0.28	-0.25	-0.25	0.15	0.57**	0.37	0.53*	0.24	-0.05	1.00			
Sm	-0.33	0.34	0.31	0.75**	0.44*	0.49*	0.30	0.18	-0.01	0.45*	1.00		
REE	-0.37	0.13	0.14	0.55*	0.45*	0.67**	0.78**	0.51*	0.25	0.72**	0.75**	1.00	
LREE	-0.25	0.04	0.08	0.46*	0.36	0.51*	0.72**	0.63**	0.38	0.70**	0.72**	0.97**	1.00
HREE	-0.60**	0.38	0.27	0.65**	0.57**	0.94**	0.68**	-0.05	-0.25	.52*	.58**	.73**	0.56*

*. Correlation is significant at the 0.05 level.

**. Correlation is significant at the 0.01 level.

In this study, average REEs were mainly represented by the LREE (Table 1). Five elements (Ce, La, Nd, Sm and Pr) recorded (78.3%) of total average rare earth elements in the studied agricultural soils. These elements concentration is mostly higher than the Chinese Background [46] of ΣREEs (154.95 µg/g) in soil. La, Nd, Sm, Y and Sc elements are positive correlate with the P, (r= 0.35, 0.15, 0.75, 0.48 and 0.56; respectively) (Table 2) this indicates that they may be derived from the use of phosphate fertilizer. Pr was positive correlate with Si (r=0.55), which indicated was derived from detrital silicate.

Gurna samples have the highest average content of LREE and HREE (193.3 and 62.4 µg/g; respectively) and the highest average values of Al, Fe and P (86787.6, 104933.3 and 12466.5 µg/g; respectively), (Table 1). Consequently, the clay minerals are important factor in mobilization the REEs and iron has the ability of scavenge them under oxidation-reduction environments in the sediments or soils [47 - 49]. In contrast, Botanic Garden samples recorded the lowest average values of the REEs, LREE and HREE (120. 2, 97.3 and 22.9 µg/g; respectively) (Table 1).

Chemical analysis data show that these elements are enrichment in the studied samples; Sm and Y (average 47.5 and 30.2µg/g; respectively) in Gurna samples, Ce, Pr and Nd in samples of the High Dam (average 76.6 , 21.9 and 28.3 µg/g, respectively) and, finally Sc and La are enrichment in Habo samples, average 30.7 and 55.41µg/g; respectively (Fig. 4). Most the studied soils are enriched with REEs than the world soil (Table 1).

3.3. Depositional Environmental and Weathering effect in Enrichment or depletion of REEs

Usually, REEs elements are mainly originated from soil parent material and rocks subjected to weathering, erosion and transportation [51]. Thus, the concentrations of REEs obviously accumulated in soils depend on the original parent material. The correlation coefficient matrix indicated that both LREE and HREE and associated with phosphate (Table 2).

Table (1) shows that LREE enrichment and HREE depletion in concentration. Thus, it revealed the effect of the weathering process. The LREE/HREE ratios (3.88) indicated the effect of weathering on REE fractionation in the studied soil. The enrichment of LREE compared with HREE was resulting of the low mobility of the former under the high power of weathering [52, 53]. Thus, the LREE/HREE ratio was increased accompanying with the high intensity of weathering. With increased weathering intensity, LREE enrichment and HREE depletion are caused by the LREE's lower mobility compared to that of the HREE [53 ,57 ,58 ,59 ,15]. Thus, the enrichment of LREE and depletion the HREE in all soils are indicated the effect of weathering processes.

As geochemical indicators of the sediment-source region, the sedimentary environment, and the post-depositional history of deposits, redox-sensitive Ce, La, Sm, and Eu, as well as, in some situations, non-redox sensitive Gd, and Y, may be used [54]. Ce can be oxidized from a Ce3+ to a Ce4+, resulting its precipitation and represented a positive Ce anomaly under oxidative conditions [55]. Positive Ce and La anomalies in the studied soils are indicated redox environment [56].

Redox conditions have no effect on REEs in natural soils. Y, La, Ce, and Pr are primarily associated with organic matter or/and Fe hydroxides and exhibit no variations between the oxic and anoxic phases [60,61]. Thus, the enrichment of them revealed the deposition under oxic and anoxic condition for the studied samples.

3.4. Sources of Rare Earth Elements

REEs can be used as a tool to identify the source rocks of the soil or sediments. Ce/La higher than (2) is indicated to hydrogenic origin and lower than (2) reveals a hydrothermal source as well as precipitated in the marine environments [62]. Ce/La ratio in the studied soil samples is (average 2.14) which is comparable to those of the average PAAS (2.13), indicating the hydrogenic origin. Most REEs are positive correlate with the P2O5, this indicates that they may be derived from the use of phosphate fertilizer and Phosphate Mining in El Sebayia for Gurna, Habo and Edfo soils. Also, Sugar, Paper and Ferrosilicon factories, Sand Quarry are affected in the enrichment of rare earth elements in Edfio soils. Finally, Botanic Garden, Fiyla and the High Dam soils are more affected from the Nitrogen Fertilizer Factory output. La/Sc ranges from 0 to 6.4 with averaging 2.8 (Table 1) which comparable to UCC (2.21, [45]), thus these REEs are related to the UCC.

3.5. REE in agriculture

The growth ability of a fussy plant depends upon some factors; plant group, their growing environment and the REEs content in the substrate soil or rock [63]. Consequently, the REEs are used in agriculture as fertilizer to improve crop growth and production. Thus, which lead to extra raise in the concentrations of REEs in soil. Very low concentrations of REEs in cereal grains (such as wheat) and no considerable accumulation from fertilization lead to wheat flour are careful to be safe [64]. Russia and Nigeria have a high natural abundance levels of REE in their soils lead to additional environmental threats arising from the increased input of REEs [65]. Thus, must be attention in the countries anywhere phosphate-based fertilizers are applied in large scale. Gurna, Habo and High Dam localities represented the high contents of LREE and HREE concentration in decreasing order. Thus, along time can be increased the accumulation of them and lead to the greater the ecotoxicity effect on crops and caused dangers effect for human health.

3.6. Pollution Indices for REEs

Although the ambiguous REEs toxicological mechanisms and related environmental hazards [66], human health, agricultural productivity and surrounding ecosystems can be adversely impacted by the presence of high REEs concentrations [67]. Many studies pointed out the adverse impact of long exposure to REEs; liver function decline [68, 69], papery oocytes [70] and endomyocardial fibrosis [71, 72]. Pollution indices help to assess the impact of REEs on the environment, their enrichment, and the contamination degree with them [73]. Pollution indices which were used in this study; enrichment factor (EF), contamination factor (CF), ecological risk (Er) and potential ecological risk index (PERI). These indices were applied widely to assess soil and sediment quality [e.g. 74, 75].

3.6.1. Enrichment Factor (EF)

EF used to evaluate the abundance of REEs in the soils /or sediments to detect the sources of them and studying their behavior in the environ [76]. The studied REEs content compare with reference elements according to [77]. EF has been estimated by the following equation according to Buat-Menard and Chesselet [78];

$$\mathbf{EF = (E_C/B_E)/(Rs/R_B)}$$

Where, Ec is the REEs concentration in the studied soil sample, BE is the background concentration of the REEs in soil worldwide [77], Rs is content of the reference metal (Zr) in the studied soil, and RB is the concentration of the reference element in soils worldwide. EF values of REEs are illustrated in figure (5a), the findings reveal that the abundance of REEs in the studied soils can be sorted in descending order depending on their EF averages into: Sm > Sc = Pr > La > Nd >Y = Ce. The studied samples show depletion in the detected REEs, except some samples with moderate enrichment of La,Pr, Nd, Sm and Sc. Only one sample show significant enrichment with Sm, and other sample show very high enrichment. This is attributed to the variation input and/or removal rate of each REEs from the soil [79 ,58 ,15].

3.6.2. Contamination Factor

Contamination factor (CF) [80] is employed to evaluate the degree of contamination of each REEs in the studied soil. The CF is calculated using the following equation:

$$\mathbf{CF = E_C/B_E}$$

The contamination factor of REEs was calculated in the soil samples (Fig. 5b), and it was found that the samples ranged from low to moderate contaminated with La, Ce, Nd and Y, recording CF value ranges 0.5-2.2, 0.2-1.6, 0.5-2 and 0.6-1.5, respectively. Samples ranged from low to considerable contaminated with Sc and Pr. The highest CF, 16.8, was recorded for Sm. Thus, the enrichment of these elements may be refers to the anthropogenic activities.

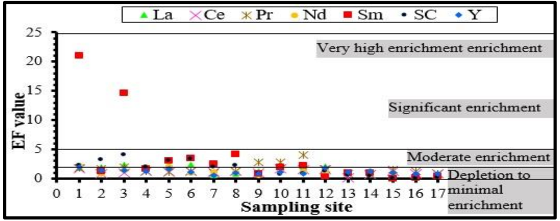
3.5.3. Ecological Risk Index (Er)

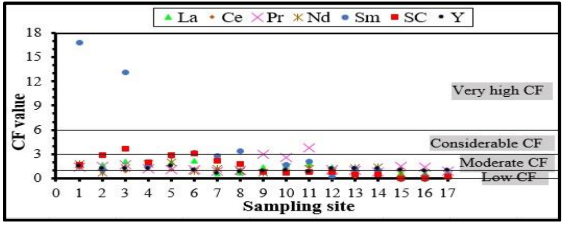
Two indices were imposed by Hakanson [80] and widely applied by many authors [e.g. 6, 8, 25, 58,81,82], to conclude the environmental risk; (a) the individual Ecological risk factor (Er), which depends on comparing the concentration of toxic elements with the geochemical background, as well as the degree of toxicity of each element, and the biological response to the level of toxicity. The other factor (b) Potential Ecological Risk Index (PERI), determines the overall environmental risks resulting from the presence of these elements in the soil. The Potential Ecological Risk Index (PERI) was calculated for soil to evaluate the potential hazard of the detected REEs on the biological systems. The Er and PERI were estimated from the following equations that described by Hakanson [80];

$$\mathbf{Er = Ti * E_C/B_E}$$

$$\mathbf{PERI = \Sigma Er}$$

Where Ti is the biological toxicity factor for each REEs, using values reported by Chen et al. [73]: La = 1, Ce = 1, Pr = 5, Nd = 2, Sm = 5, Eu = 10, Gd =5, Tb =10, Dy = 5, Ho = 10, Er = 5, Tm = 10, Yb = 5, Lu = 20, Y = 2, Sc = 2. Where, Cn is REEs content in the soil sample and Bn is the background concentration of the REEs in soil worldwide [77]. The values of ecological risk factor (Er) in the studied soil samples are given it figure (5c). The results show that the Er degree of REEs can be arranged in descending order Sm > Pr > Sc > Nd > Y > La >Ce. Where all the Er values are < 40 indicating low ecological risk, except samples No. 1 and 3 which show considerable and moderate ecological risk, respectively with Sm (Fig. 5d). On the other hand, the obtained PERI data shows that the studied soils ranged from 11.3 to 103.7 indicating low PERI.





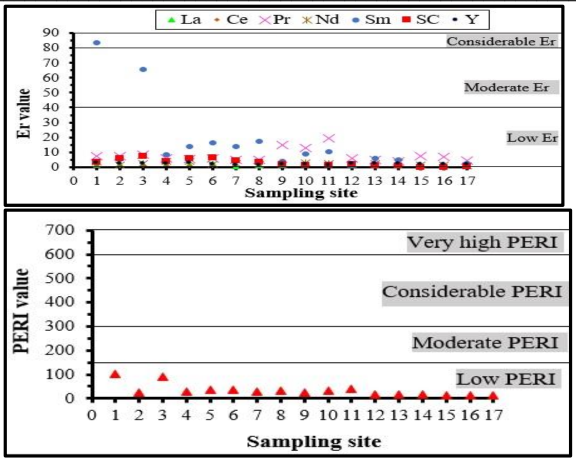


Fig. 5. Pollution indices of the studied REEs in soil (a) EF, (b) CF, (c) Er and (d) PERI.

4. Conclusions

The environment can be contaminated with diverse types of toxic inorganic, organic, and organometallic types, which is one of the majority solemn problems in the world nowadays. The REEs assembly considered vital elements originates in the environment. Thus, it requests to be studied at superior to understand their effects on human health. REEs accessibility and toxicity depended on the sediment composition. So, the relatively higher LREE/HREE fractionation in studied agricultural soils formed under the warm zone was possibly resulted the abundance of montmorillonite. Ce/La revealed the hydrogenic origin for the studied agriculture soils. Gurna, Habo and High Dam localities are represented the high contents of LREE and HREE concentration in decreasing order. With long time may be more the gathering and lead to the greater the ecotoxicity effect on crops and might be deleterious for human health. The study characterizing of clay content in the agriculture soils of Luxor and Aswan governorates reveals that they are the important factor controlling both REEs availability and toxicity elements.

5. Recommendations

The following are recommended:

- A detailed baseline study about the distribution of potential toxic elements in the Egyptian environmental constituents (soil, water, air and plant) must be done.
- Transport the industrial zone into the rejected lands in the desert.
- Use of eco-friendly agrochemicals (fertilizers, pesticides and herbicides).
- Systematic certification of impact on crops, animals and humans should be taken in consideration to improve agricultural productivity and human health.
- More importantly, government should present funds accessible for research of environmental geochemistry and to employ data so generated in mine planning.

6. Conflicts of interest

There are no conflicts to declare

7. Formatting of funding sources

No fund.

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