



## Central Nile Valley agriculture soil content and distribution of rare earth elements (REEs), Egypt



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The Nile Valley hosted the world's oldest civilizations because of the quality of the agricultural soil and the waters of the Nile River. Despite the importance of the Egyptian agricultural soil, there is a scarcity of information about its chemical and mineral composition. Therefore, this research is concerned with the soil content of rare earth elements (REEs), as it has become one of the elements with a harmful effect and considered emerging contaminants. The concentration of only 6 REEs were recorded in the agricultural soil of Assiut Governorate; Sc, Y, La, Ce, Sm and Nd with concentrations 26.6, 22.2, 33, 62.2, 8 and 30.6  $\mu\text{g/g}$ , respectively. However, the average REEs (182.6  $\mu\text{g/g}$ ) was higher than the upper continental crust (179.4  $\mu\text{g/g}$ ), world soil (145.3  $\mu\text{g/g}$ ), Chinese soil background (163.86  $\mu\text{g/g}$ ). This indicates the enrichment of the Egyptian soil with these elements. This enrichment may be due to the nature of the source rocks or the applied fertilizers. Where phosphate fertilizers (rich in elements) are applied frequently to improve soil productivity.

**Keywords:** Rare earth elements; Nile Valley soil; Pollution indices; Anthropogenic; Natural source.

### 1. Introduction

The rare earth elements consist of the lanthanide group, in addition to scandium and yttrium. These elements are found in more than 200 minerals worldwide (Henderson, 1984). REEs have similar chemical properties (Ferreira et al., 2022) and can be divided into two groups of light (La to Eu) and heavy (Gd to Lu) REEs (Maulana et al., 2014). Because of the unique characteristics of the REEs, which improved the yield and quality of agricultural products when applied in nano-fertilizers (Boyko et al., 2011; Zhuang et al., 2016; Huang et al., 2019), but it was observed that it resulted in different physiological effects (Positive or negative) (Zhang et al., 2013) where it was observed that the use of micro-fertilizers containing high concentrations of rare earth elements may be harmful to the ecosystem (Barry and Meehan, 2000), and long-term exposure to REEs, biota organisms may be harmful, it is also involved in human respiratory system (Censi et al., 2011), liver function (Arvela et al., 1977; Zhu et al., 2005),

nervous system (He et al., 2008; Zhu et al., 2005), and gastrointestinal tract. and circulatory and immune systems (Zhang et al., 2000), as well as the intellectual system of children (Fan et al., 2004). Technological progress has become the characteristic of the modern era, which relies heavily on the use of rare elements (Lima and Ottosen, 2021) due to their superior physical and chemical properties. However, their environmental instability and toxicity has become a major environmental problem (Gwenzi et al., 2018; Li et al., 2020), so these elements are considered emerging pollutants. Soil is the main link in the food chain, and its enrichment with these elements can expose organisms and humans to serious health problems (Gwenzi et al., 2018; Li et al., 2013). River Nile is the longest river worldwide and passes through 11 countries. Egypt is the downstream country of the Nile Basin, in which the oldest civilizations was established because of the fertility of the soil in the Nile Valley. The environmental security of the River Nile is of great significance to Egypt. Assiut Governorate is of great importance because of

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it contain some big industrial activities (Cement, Fertilizers, and petroleum), beside agricultural activities (Abou El-Anwar et al., 2019a). The rapid economic and urban development in the Nile Valley led to the emergence of heavy metal pollution in the agricultural soil, surface and ground water, and plants due to human activities (Mekky et al. 2019; Salman et al. 2017). The integrity of the soil environment in the Nile Valley is of great importance to the growth of the agricultural economy and the health of living organisms and humans, so it is important to study the concentrations and environmental effects of REEs due to the global interest in these elements as emerging pollutants. As, it was found high concentrations of these elements in Egyptian phosphate ores (Abou El-Anwar et al. 2019b). Pollution indices were applied widely to study the enrichment of elements in soil and sediment to discriminate element source and adverse environmental impact (Abou El-Anwar et al. 2021; Elnazer and Salman 2021; Mostafa et al. 2023). The current study aims to investigate the occurrence of REEs in Agricultural soil in Assiut Governorate, discriminate their spatial distribution, source and enrichment degree.

## 2. Materials and Methods

### 2.1. Study area

Assiut Governorate is a part of Nile Valley, nearly located in its center between latitudes 26° 50' and 27° 40' N and longitudes 30° 40' and 31° 32' E (Fig. 1). It contains the old cultivated land, the desert fringes reclaimed land, the limestone plateaus on both banks of the Nile River. The governorate characterized by intensive human activities; urbanization, contain Two universities in addition to big industries (cement, fertilizers, and pharmaceutical, power station, detergents). As a part of the Nile Valley, the study area geology has been investigated by many authors (e.g. Said 1962 and 1981; Omara 1972; Youssef et al. 1977; Omer 1996; Osman 1980). The area composed of sedimentary succession ranges from Tertiary to the Recent (Fig. 2). The soil of the study area is mainly originated from the Ethiopian high lands and Red Sea Mountains (Omer 1996). The source rock and land use control the chemistry of soil at Assiut (Mekky et al. 2019).

### 2.2. Sampling and analyses

The agricultural soil from north Assiut city was sampled from 16 sites (30 cm depth) (Fig. 1). About 1 kg. of soil was collected from each site with clean stainless-steel shovel, packed in polyethylene bags,

labeled and transferred into Geological Sciences Dept. lab, National Research Centre. At the lab, the samples were air dried for 5 days until constant weight, then each sample sieved with 2 mm sieve, the sample was humanized and subsample was pulverized into <63µm for analyses. The XRF (Axios Sequential WD\_XRF Spectrometer) was used to determine the element content of soil samples.

### 2.3 Pollution indices calculations

Five pollution indices were applied in this study;

The enrichment factor (EF) is given by the following equation (Sutherland 2000):-

$$EF = (C_m/B_m) / (R_s/R_c)$$

The index of geoaccumulation ( $I_{geo}$ ) was calculated by the following equation (Muller 1979):-

$$I_{geo} = \text{Log}_2 (C_m/1.5*B_m)$$

The Contamination Factor (CF), Ecological Risk Factor ( $E_r$ ), and Potential Ecological Risk Index (PERI) were determined using the following equations (Hakanson 1980):-

$$CF = C_m/B_m$$

$$E_r = T_r * CF$$

$$PERI = \sum E_r$$

Where,

$C_m$ : the examined element in the soil,

$B_m$ : the examined element content in the world soil,

$R_s$ : the reference element content in the soil (in this study “Zr” used as  $R_s$  because it is mainly of natural lithogenic source (Blaser et al. 2000; Bam et al. 2011))

$R_c$ : the reference element content in the world soil.

**The constant 1.5:** is used for the possible variations of the background data due to the lithogenic effects.

**Table 1. REEs mean in worldwide soils (After Kabata-Pendias and Mukherjee 2007) and the toxic-response values (After Chen et al. 2020).**

Element	World Soil Average ( $B_m$ ) mg/kg	Toxic-response (Tr)
Sc	9.5	-
Y	12	2
La	26.1	1
Ce	48.7	1
Nd	19.5	2
Sm	4.8	5
Zr	300	-

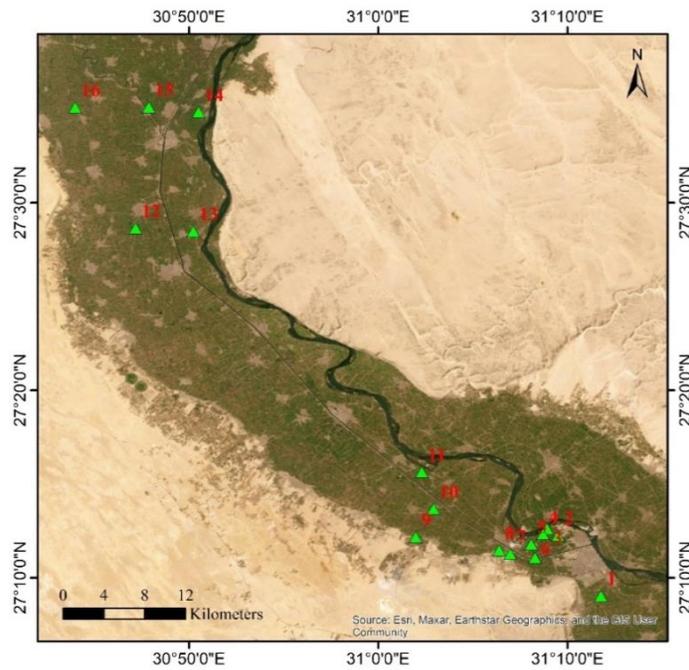


Fig. 1. Location map of the study area showing sampling sites.

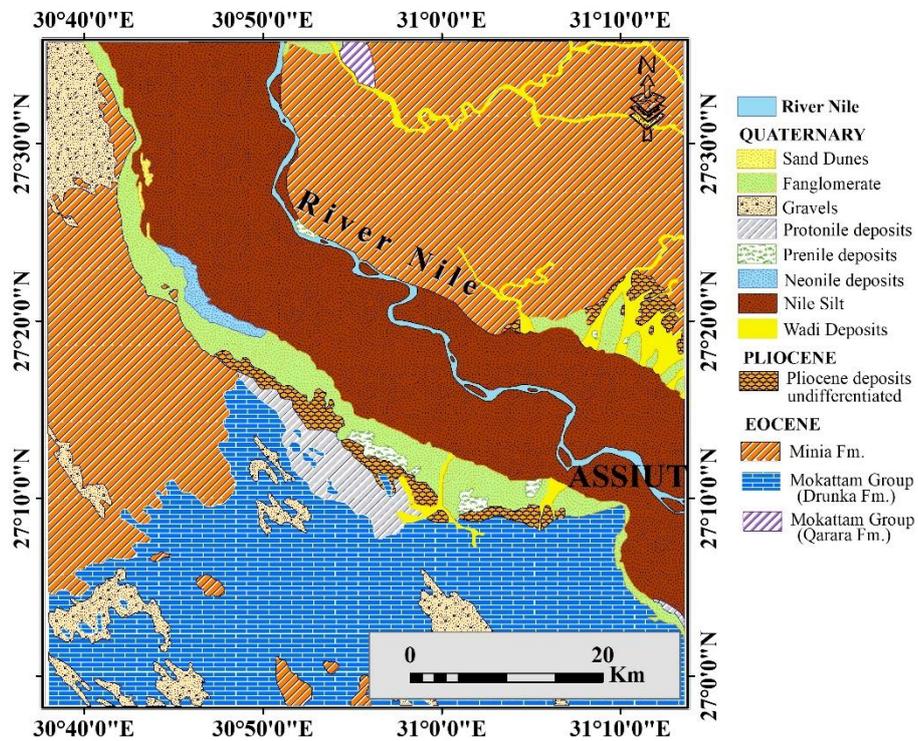


Fig. 2. Geologic map of the study area (After Conoco 1987).

The spatial distribution maps of studied elements were created by using ArcGIS 10.2 software (Inverse distance weighting (IDW) tool). This technique has been used to conduct environmental monitoring, understand and predict pollutant spread (Salman et al. 2019 and 2021, Salman and Elnazer 2020).

### 3. Results and Discussion

#### 3.1. Petrographic study

The mineralogical analysis of the studied samples deals mainly with heavy minerals. Heavy minerals are used as guide to source rock lithology. Heavy minerals content not only controlled by the source rock lithology, but also by weathering operating

process, transport, deposition and diagenesis (Morton and Hallsworth, 1994). Under polarizing microscope, heavy minerals of the studied samples are consisted mainly of opaque minerals. The non-opaque minerals are zircon, epidote and rutile (Fig. 3). Zircon is the most dominant mineral in this group. It occurs as colorless prismatic, rounded and subrounded grains. Some zircon grains are fractured and contain inclusion. Epidote is found as pal green color. Rutile grains is characterized by reddish-brown color, high relief with sub-rounded edge.

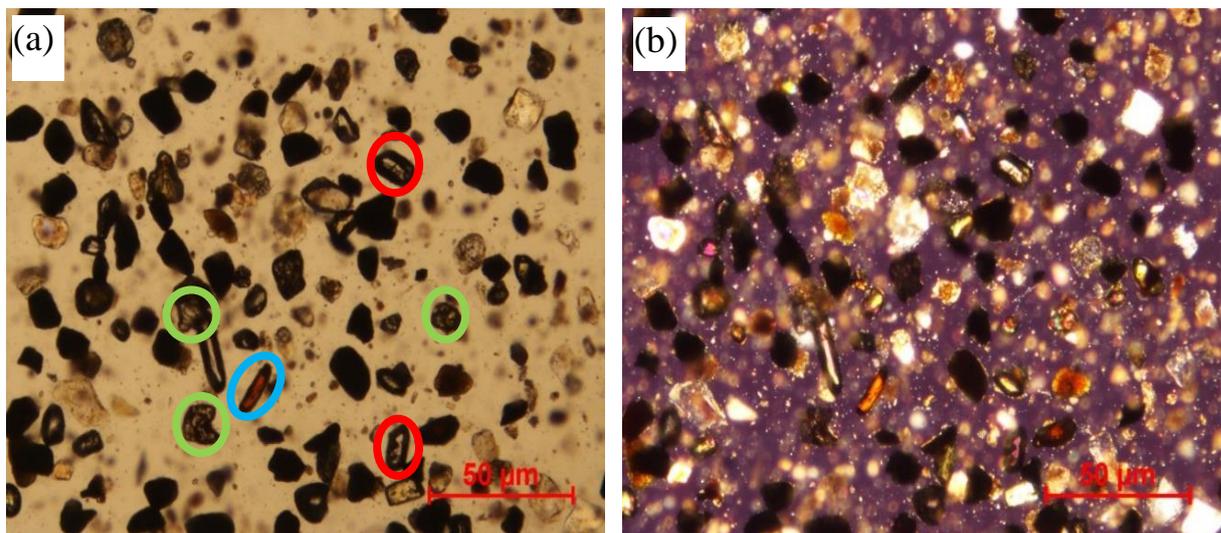


Fig. 3. Microscopic photos showing mineral distribution in the studied soils (a) under PPL 4X (b) under CN 4X. Red circle showing euhedral to subhedral zircon showing prismatic shape, green circle showing epidote grains are mainly prismatic with yellowish pale green color and Blue circle showing Elongated subhedral red coloured rutile grains.

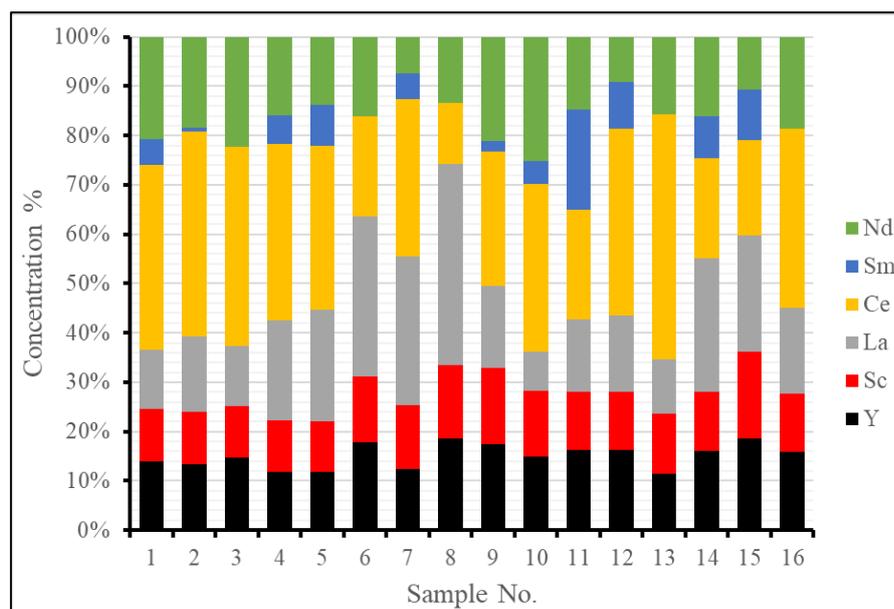


Fig. 4. Distribution pattern of REEs in the studied samples.



### 3.2. Concentrations and distribution patterns of REEs in the soils

Concentrations of REEs and characteristic of Nile Valley soils were given in Table (2). The average concentrations of REEs in the studied soils followed decreasing order of  $Ce > La > Nd > Y > Sc > Sm$ , which followed the Oddo-Harkins rule (Wei et al., 2001). Hence, the increased concentrations of La and Ce in the soil need attention because their enrichment may lead to bioaccumulation, as happened in maize plants (Galhardi et al., 2020). Ce, with an average concentration of 62.2  $\mu\text{g/g}$ , is the prevailing among the recorded REEs, and represent 31.2% of total REEs (Fig. 4). Sm recorded the lowest concentration in the studied soil (8  $\mu\text{g/g}$ ), which represents 5% of the total concentration of the recorded REEs. REEs sources in the environment may be attributed to rock weathering, mining and industrial process, fertilizers and pesticides, while pathways include soil, water, animal and human (Fig. 5). The concentrations of detect 6 REEs; REEs ranged from 87.9 to 342.3  $\mu\text{g/g}$ , with an average value of 182.6  $\mu\text{g/g}$ . The REEs in the studied soils was higher than the upper continental crust (179.4  $\mu\text{g/g}$ ) (Taylor and McLennan, 1995), world soil (145.3  $\mu\text{g/g}$ ) (Kabata-Pendias and Mukherjee 2007), and Chinese soil background (163.86  $\mu\text{g/g}$ ) (General environment monitor station of China., 1990). The  $\Sigma\text{REEs}$  in Egypt's soil was 182.6 mg/kg; is higher than the average concentrations in the Earth's crust, Chondrite, Germany, Brazil, Europe, Cuba and China, but only lower than those in Central Africa (Cameroon) (Table 3). These results indicate that the REEs are slightly enriched in the agricultural soil in Assiut. This enrichment may be a result of the parent rocks of soil, as a result of the pedological processes of the soil itself and/or human activities (such as fertilizers and pesticides).

A significant positive interrelationship was recorded between the recorded REEs (excluding Sm) as indicated by the Spearman's correlation analysis, with a correlation coefficient from 0.02 (La vs. Nd) to 0.91 (Sc vs. Y) (Table 4). The strong positive interrelationship between the REEs indicates their similar sources. The Nile Valley soil is mainly derived from the mafic/ultramafic rocks of the Ethiopian high lands (Omer 2003). This source

rocks are enriched with REEs (Yibas et al., 2003). Also, these close relationships between the REEs suggests the coexistence and similar REE sources during geochemical processes (Gwenzi et al., 2018, Temga et al., 2021). Sm exhibited no significant correlation with the recorded REEs (Table 4). In fact, Sm is present in fertilizers that are widely used in Egypt (Abou El-Anwar et al. 2017). Therefore, Sm poor correlation with other REEs is attributed to its anthropogenic inputs into soils.

### 3.3. Spatial distribution of REEs

Spatial distribution maps are maps that use cartographic representation methods to clarify spatial relationships between distributed phenomena (concerned with clarifying the spatial pattern) on maps. It gives a true picture of economic, environmental or geological...etc. problems, and hence provides ease in scientific representation and analysis. These maps are considered more accurate and more useful than the traditional descriptive methods, by representing the quantitative results on the maps to show the spatial variation in the distribution of the studied phenomena (e.g. element concentration distribution) (Salman et al. 2019a,b&c; Salman and Elnazer 2020; Seleem et al. 2021; Salman et al. 2021). The distribution map of the recorded REEs (Fig. 6) in Assiut depicts variation in REEs distribution with observed higher concentration in the north and lower contamination in the central part. Based on their spatial distribution patterns, Y, Sc, La, Ce and Nd have slightly close distribution, while Sm has unique distribution. This spatial distribution of REEs can give information about element source and identify highly contaminated areas. The main source of REEs in the study area is the parent rock weathering, where the studied soil contains many REE-bearing minerals such as zirconium and rutile. The REEs source rock in Egypt are mainly black sands, phosphorites and granites (Fig. 7) (Baoumy 2021). Phosphatic fertilizers are applied widely in Egypt for enhancement soil productivity. Phosphorites are extracted for industrial application (e.g. fertilizers production) from the Red Sea, Nile Valley, and Abu-Tartur regions in Egypt. The REEs in these phosphorites are 684.6, 212.8 and 165.6 mg/kg for Abu-Tartur, Red Sea and Nile Valley respectively (Baoumy 2021).

**Table 3. Mean REE concentration in Egypt's soil compared to international soil data.**

Country	Y	Sc	La	Ce	Sm	Nd	ΣREE
Present	26.6	22.2	33.0	62.2	8.0	30.6	182.6
EC Wedepohl (1995)	24	16	30	60	5.3	27	162.3
Chondrite Pourmand et al. (2012)	1.4	5.5	0.247	0.632	0.156	0.485	8.42
Germany Mihajlovic et al., 2017	8.99	2.67	18.66	40.98	3.77	18.99	94.06
Brazil Silva et al. (2016)	4.45	2.31	20.8	43.5	3.37	17.7	92.13
Europe Sadeghi et al. (2013)	-	-	25.9	52.2	4.28	22.4	104.78
Cuba Alfaro et al., 2018	-	-	15.2	24.2	4.40	17.1	60.9
China (Wei et al. 1991)	-	-	37.4	64.7	4.94	25.1	132.14
Cameroon Temga et al. 2021	-	-	58.16	134.32	8.59	64.73	265.8

**Fig. 5. Sources and pathways of REEs.**

### 3.4. Pollution indices

Several factors have been applied to study the extent of soil pollution and its enrichment with REEs; CF, Igeo and EF (Table 2). The CF values ranged from 0 for Sm to 4.4 for Sc. It was observed that Y and Sc have the highest CF among the recorded REEs. The descending order of the calculated values of Igeo indicated that the soil was unpolluted with La and Ce, and that it was unpolluted to moderately polluted with the rest of REEs.

The EF is one of the strongest evidences of soil pollution, where a reference element resistant to various weathering processes is used to obtain the best results and evidence of the role of human factors in soil pollution, separating it from natural factors. The highest and lowest value for the EF was recorded for Sm.

elements in terms of the CF was as follows: Sc>Y>Sm>Nd>La=Ce.

The Igeo is one of the most important indices for studying the extent of soil contamination with Potentially toxic elements, which has been applied since 1979 until now to assess soil pollution with various elements. The average

### 3.5. Ecological risk of REEs

In plants, the ecotoxicological of REEs includes reduced plant growth, genotoxicity and neurotoxicity in animals, and kidney damage, nervous system dysfunction, lung enlargement, male sterility, and fibrous tissue injury in humans (Gwenzi et al., 2018).

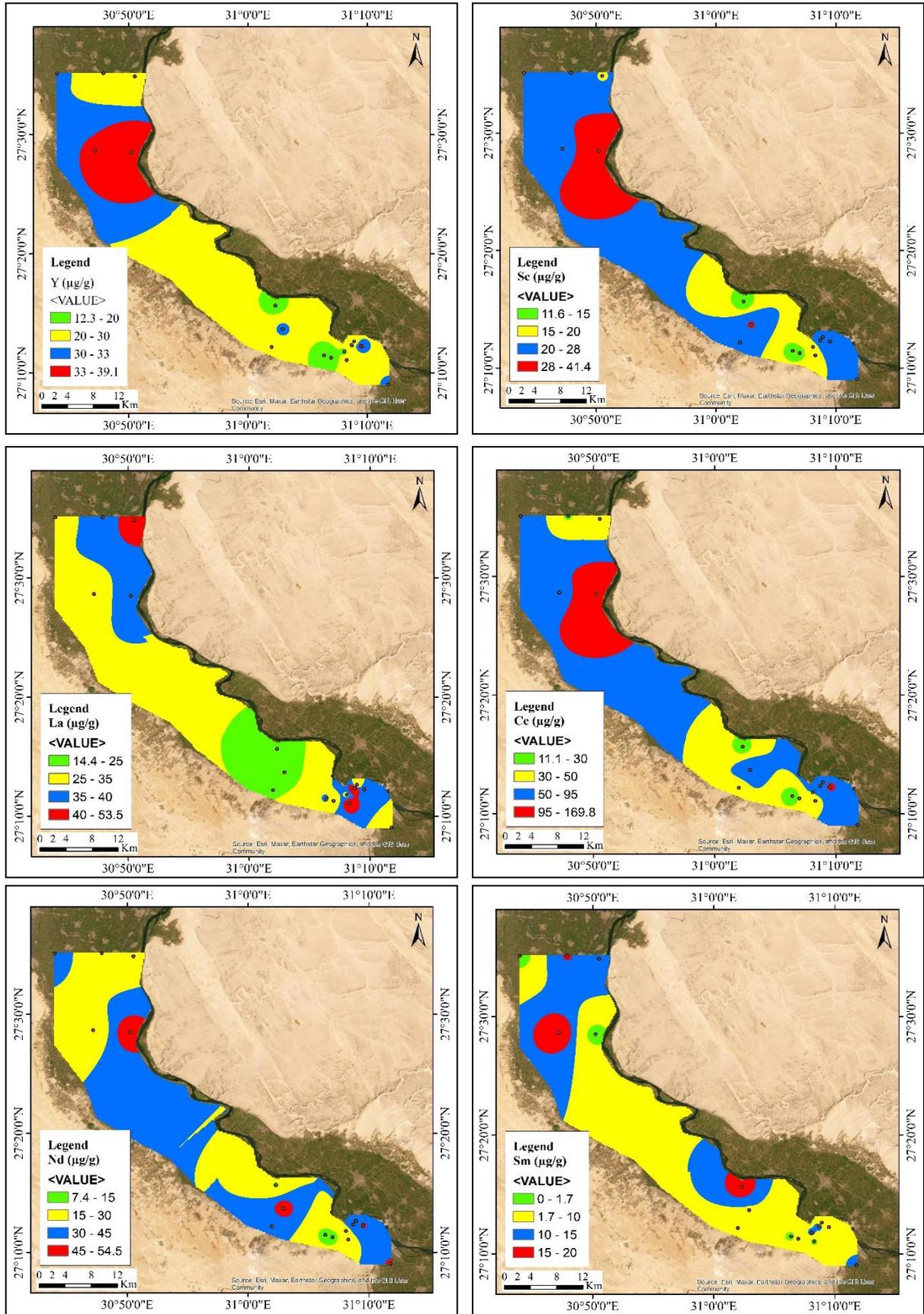
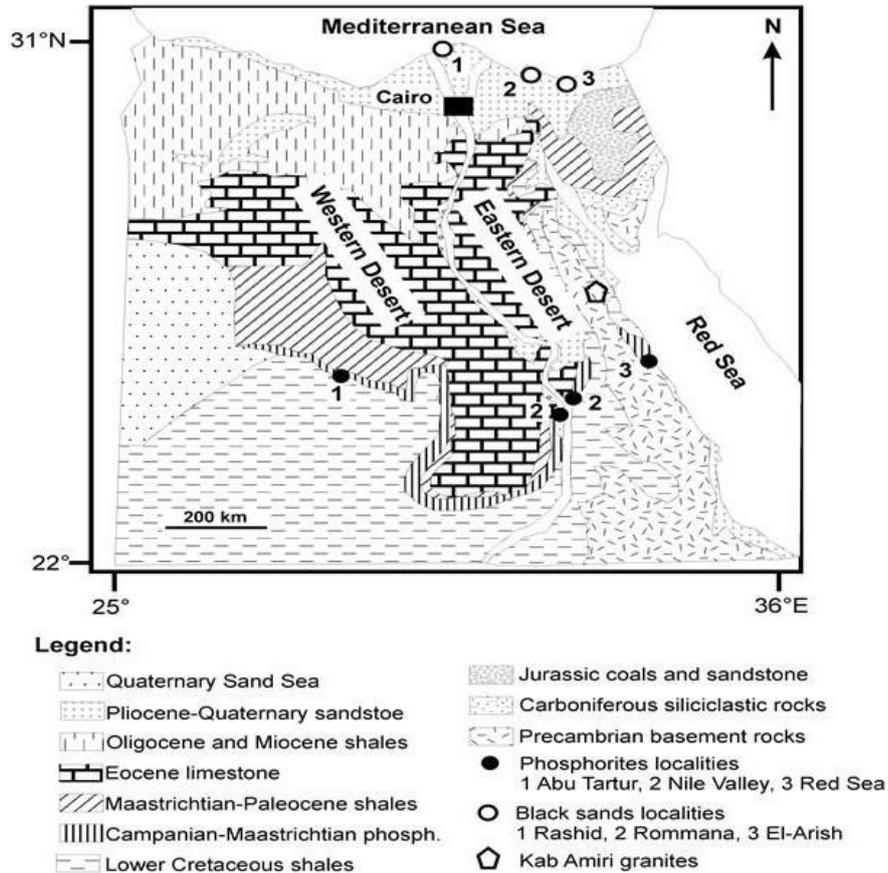


Fig. 6. Spatial distribution maps of the recorded REEs.



**Fig. 7. Distribution of REEs source rock in Egypt.**

The Er of the individual REEs in Assiut soils were arranged in decreasing order as follow: Sm (8.4) > Y (4.4) > Nd (3.1) > La (1.3) = Ce (1.3) (Table 2). The PERI ranged from 5.5 to 30.3 with average value 18.5 (Table 2). Both of Er and PERI indices was <40 and <150, respectively, indicating the low risks caused by REEs. Ecological risk assessment is one of the most widely used theoretical methods for evaluating the risks posed by the presence of harmful elements in the environment. It depends on the concentration of the element in the soil, the value of the environmental background, and the toxicity response coefficient of the element. Where human health depends on the agricultural sector as the most important link in the food chain. Therefore, the assessment of soil pollution and the resulting health risks has become one of the most

important studies for a sustainable healthy life, and because soil quality is essential for food safety.

#### 4. Conclusion

The concentration of elements in the agricultural soil of Assiut governorate was relatively high compared to the global soil. The spatial distribution of the elements differed, with hot spots appearing in the north of the study area for all REEs, while hot spots appeared in the south for La, Nd and Sm. Pollution indices showed that the soil pollution with REEs was low to medium in most sites. Fortunately, the occurred concentrations of REEs haven't emergence ecological risk in the study area.

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**Contribution of Authors:** All authors shared in writing, editing and revising the MS and agree to its publication.

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## توزيع العناصر الأرضية النادرة في التربة الزراعية بوسط وادي النيل، مصر

### ربط الجيولوجيا التركيبية و جيولوجيا البترول

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قامت على وادي النيل أقدم الحضارات وأعرقتها في العالم بسبب خصوبة التربة وجودتها. وبالرغم من أهمية التربة الزراعية إلا أن تركيبها الكيميائي والمعدني ومحتواها من العناصر الأرضية النادرة لم يحظى بالكثير من الاهتمام، ولذلك فإن هذا البحث يهتم بمحتوى التربة من العناصر الأرضية النادرة، حيث اتضح إنها ذات تأثير ضار على صحة الإنسان والكائنات الحية. أظهرت الدراسة الميكروسكوبية (البترولوجرافي) للتربة أنها تحتوي على المعادن الثقيلة مثل: الزيركون والأبيدوت والروتيل، كما أوضحت التحاليل الكيميائية وجود ٦ عناصر أرضية نادرة بالتربة الزراعية بأسيوط Nd, Sc, Y, La, Ce and Sm بتركيزات (٢٦,٦، ٢٢,٢، ٣٣، ٦٢,٢، ٨، ٣٠,٦) ميكروجرام / جرام على التوالي، وكان المتوسط الكلي للعناصر الأرضية النادرة ١٨٢,٦ ميكروجرام / جرام أعلى من القشرة القارية والتربة في الصيني ١٧٩,٤ و ١٦٣,٨ ميكروجرام / جرام، وقد تكون الزيادة في العناصر الأرضية النادرة في التربة بأسيوط نتيجة من الصخور المصدر أو الأسمدة المستخدمة، حيث تستخدم الأسمدة الفوسفاتية (الغنية بالعناصر الأرضية النادرة) في هذه المناطق بشكل متكرر لتحسين إنتاجية التربة. اختلف التوزيع المكاني للعناصر الأرضية النادرة حيث تركزت معظمها في شمال منطقة الدراسة، بينما تركيزات Sm, Nd, La في الجنوب، وأظهرت معاملات التلوث أن تركيزات العناصر الأرضية النادرة لا تشكل خطر بيئي بمنطقه الدراسة.