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# VERTICAL DISTRIBUTION OF MAJOR AND TRACE ELEMENTS IN A SOIL PROFILE FROM THE NILE DELTA, EGYPT

**Abstract:** The present study was conducted to highlight the elemental composition of ten soil samples collected at different depths along of a soil profile (0.25-17 m). The collected samples were subjected to epithermal neutron activation analysis at the pulsed reactor IBR-2 of Frank Laboratory of Neutron Physics - Joint Institute for Nuclear Research - Dubna - Russian Federation. The concentrations in mg/kg of 36 major and trace elements were determined. Symbatic behaviour of geochemically related elements was observed: Th and U; Cl and Br and Fe, Ti, Ca, Al, and Mg, etc. A sharp increase of certain concentrations at the depth of 8 m was observed. Significant mafic sources of elements were observed and mostly are attributed to Ethiopian High Plateau with small amount of felsic volcanic rocks.

Keywords: Nile Delta, INAA, soil profile, major and trace element

### Introduction

The Nile Delta extends to an area of about 22,000 km<sup>2</sup> and accounts for two-thirds of Egypt's agriculture [1-3]. The Nile Delta is part of the Egyptian Mediterranean coast and extends approximately 240 km from Abu Quir headland at Alexandria in the west, to Port Said in the east [4]. The concentration of Egyptian population in less than 5 % of the country's land area has resulted in the lowest arable land per capita of any country in Africa [5], and has driven Egypt to further expanding its cultivated area by perennial irrigation along the Nile valley and in the Delta. The Nile delta is an agriculture area and it provides 63 % of the country's agricultural land. The Nile Delta coastline has two promontories, Rosetta and Damietta. In addition, aluminium it has beaches that are backed by coastal flats followed by coastal dunes and four brackish shallow lakes (namely: Mariut, Edku, Borullus, and Manzalah) [6]. The severe industrial and agricultural influence on coastal wetlands at the Nile Delta - Egypt and specifically for the urban lakes at the north coastal areas of the Mediterranean Sea were comprehensively investigated by Keshta, Shaltout [7] to show considerable amounts of Co, Cu, and Cr in Edku lake. The Aswan High Dam (AHD) was completed in 1964, and aimed to produce clean energy and to conserve and protect the agriculture in Egypt by controlling the Nile floods. However, it had a dramatic

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negative effect on the sediment flux to the Delta. Since that time, the supply of sediment reaching the river mouth at Rosetta and Damietta has no longer been sufficient to stabilize the delta coastline and prevent coastal erosion [8]. Stanley [1] and Hamza [8] confirmed that neither the blockage of the Nile flow at Aswan, nor additional influence of natural factors including subsidence, sea-level rise, and near shore current processes could fully explain the altered sedimentary regime currently prevailing along the Nile Delta coast. Stanley [1] suggested that the trend of land loss along the Delta margin may be explained by increased sediment entrapment in the Delta proper, between Cairo in the south and the coast in the north. An important environmental problem in the Nile Delta is the entrapment of sediment in Lake Nasser behind the High Dam, which leads to an increased consumption of chemical fertilizers, insecticides and pesticides for agriculture soil. As silt is no longer available, toxic and radiative elements will migrate in the soil profile and in turn to the ground water. Because of silt and clay minerals are composed mainly of plate-like secondary aluminium silicate with small particle size and a negative charged surface, therefore silt particles have the ability to absorb cations on their surface [9]. Measuring the concentration of metals, the associated pollution indices, and the ecological hazards in soil and sediments have attracted the attention of several researchers for instance [2, 10-15].

The present work is an attempt to study the vertical distribution of major and trace elements in a soil profile in the Nile Delta to extract more information about the geochemical characteristics of soils and sediments. The assessment of the elemental composition of soil profile at different depths provides a baseline data for establishing predictable long-term and widespread changes in soil and groundwater quality. In addition, having such data helps in evaluating the anthropogenic influence on soils and sediments.

The objectives of this study were to describe, evaluate, (mutli-elemental) analyse, and compare the vertical distribution of these elements in samples collected from the Nile Delta soil profile. To achieve these objectives, a high-precision, sensitive, and non-destructive Instrumental Neutron Activation Analysis (INAA) was used and a total of 36 elements were determined in soil profile at different depths ranging from 0.25 to 17 m in the Nile Delta - Egypt.

# Material and methods

#### Study area and sampling

The samples were collected in 2016 at a site with latitude 30°32' N and longitude 31°16' E, near the city of Kafr Shoukr. This city is located in the Nile Delta, ~50 km north-west of Cairo, not far from the Damietta distributary. Ten samples of approximately 1 kg each were collected from a soil profile (0.25-17 m depth). The samples were packed, coded and transferred to the laboratory in the National Research Centre of Egypt. Next, the samples were air-dried, cleaned from extraneous materials and vegetation, well mixed, crushed, and homogenized in a non-iron grinder (mortar bowl and pestle) to avoid contamination of the samples with iron. Then, the samples were sieved to get homogeneous grain size of particles  $\approx 2$  mm mesh for each soil layer. Few grams of each samples from each depth were packed separately and sent to Frank Laboratory of Neutron Physics (FLNP), Joint Institute for Nuclear Research (JINR) for analysis by means of epithermal neutron activation analysis ENAA. More details about the preparation of the collected soil samples were reported by Arafa et al. [2] and Badawy et al. [12].

### Analytical methods

Epithermal neutron activation analysis (ENAA) was performed at the reactor IBR-2M of FLNP-JINR, Dubna, Russia. Samples of about 0.1 g of soil were wrapped in polyethylene packs or in aluminium cups for short- and long-term irradiation, respectively. To measure the short-lived isotopes, the wrapped samples in polyethylene were packed in polyethylene containers and irradiated via the pneumatic system. The duration time of irradiation is 60 s and then measured by using High Purity Germanium detector (HPGe) for 15 minutes. While the samples in aluminium cups were put in aluminium containers and irradiated for 3-4 days. Next, they were repacked, and then measured twice to obtain two groups of long-lived isotopes. To measure the first group of long-lived isotopes, the repacked samples were cooled for 4-5 days and measured for 30 minutes. For the second group of long-lived isotopes, they were cooled for 20-23 days and measured for 1.5 hour. More details about the used analytical scheme and neutron flux and irradiation channels are described by Badawy et al. [10], Frontasyeva [16], Pavlov et al. [17], Pavlov et al. [18], Badawy et al. [12] and Arafa et al. [2]. Gamma spectra processing and elemental concentration determinations were performed using proprietary software developed at FLNP [18]. Characteristics of measured elements in short and long-lived measurements in NAA - Pulsed Reactor IBR-2M at FLNP-JINR are given in Table 1 SM (see Supplementary Materials).

#### **Quality control**

Quality control was provided by simultaneous analysis of the following NIST Standard Reference Materials: 2709 - San Joaquin Soil, 2710 - Highly Elevated Trace Element Concentrations Montana Soil, 2711 - Moderately Elevated Trace Elements Concentrations Soil, 1633b - Constituent Elements in Coal Fly Ash, 1632c - Trace elements in coal, as well as IAEA Certified Reference Material: 433 - Marine Sediments.

Blank analysis was carried out using blank polyethylene container in short-lived irradiation of samples and influence on the concentration of the elements was not noticed. While in case of long-lived irradiation, the samples are wrapped in Al-foil.

Software packages OriginLab<sup>TM</sup> Origin 8.5, MS<sup>TM</sup> Excel, and R Project for Statistical Computing [19] were used for data analysis and graphing. Principal Component Analysis PCA was implemented.

### **Results and discussion**

Concentrations of 36 major and trace elements in the soil profile (0.25-17 m depth) were determined by means of epithermal neutron activation analysis (ENAA). Mean, median, standard deviation, minimum and maximum values are shown in Table 1 and concentrations of the elements for each depth and the corresponding uncertainties (mean  $\pm$  *SD*) are given in Table 2 SM (see Supplementary Materials). The descriptive statistics of the obtained results are illustrated in Figure 1. The obtained results were compared with corresponding mean values reported by Rudnick and Gao [20] for Upper Continental Crust (UCC) and Viers et al. [21] for average world suspended sediment (AWSS). A total of 22 out of 36 elements are slightly higher than the compared values for UCC reported by Rudnick and Gao [20]. These elements can be given in descending order as: Br > Ti > Mg > Zr > Hf > Eu > Cl > Tb > Fe > Nd > Nb > La > Ni > Yb > V > Mn > Tm > Cr > Ce > Co > Zn > Ba. Whereas, 14 out of the 36 elements were lower than the

corresponding values in UCC. These elements are Al, Sr, Sc, Ca, Si, Rb, Mo, As, Ta, Cs, U, Na, Th, and Au.

Table 1

Mean, median, standard deviation, minimum, and maximum concentrations regarding the distribution
of 36 major and trace elements in soil profile. For comparison, the corresponding values were given as reported
in literature for mean Upper Continental Crust (UCC) [20], average world suspended sediment (AWSS) [21]
and Shapiro-Wilk test of normality were calculated at a significant $p = 0.05$ . All concentrations
were expressed in mg/kg, unless otherwise stated

Element	Mean	Median	SD	Min.	Max.	UCC [20]	AWSS [21]	Statistics	<i>p</i> -value
Na [%]	0.98	0.95	0.43	0.45	1.83	2.42	0.71	0.94	0.57
Mg [%]	3.27	3.27	1.30	0.66	5.88	1.50	1.26	0.91	0.26
Al [%]	7.30	7.25	2.59	1.90	10.30	8.15	8.72	0.93	0.41
Si [%]	26.06	26.95	9.97	5.92	39.40	31.13	25.4	0.96	0.83
Cl	372.2	297	256	137	1010	244	ND	0.80	0.01
Ca [%]	2.19	2.11	0.96	0.50	4.39	2.56	2.59	0.88	0.12
Sc	19	21	7	2.4	26	22	18	0.84	0.05
Ti [%]	0.92	1.04	0.43	0.14	1.86	0.38	0.44	0.89	0.16
V	171	177	73	21	311	138	129	0.91	0.31
Cr	159	163	58	24	254	135	130	0.88	0.13
Mn	943	979	366	197	1490	774	1679	0.97	0.91
Fe [%]	5.51	6.17	2.08	0.66	7.60	3.92	5.81	0.84	0.04
Ni	78	84	20	41	98	59	75	0.87	0.09
Со	28	31	10	4	40	27	23	0.79	0.01
Zn	75	82	29	8	99	72	208	0.80	0.02
As	2	2	1	0.2	4	3	36	0.94	0.50
Br	7	2	7	0.2	17	1.6	22	0.78	0.01
Rb	40	44	13	12	52	49	79	0.86	0.07
Sr	276	254	101	82	468	320	187	0.94	0.50
Zr	247	265	68	99	357	132	160	0.88	0.12
Nb	11	11	3	4	15	8	14	0.88	0.15
Мо	0.6	1	0.3	0.1	1	1	3	0.91	0.25
Ba	476	414	155	225	745	456	522	0.94	0.51
Cs	1.2	1	0.7	0.1	2	2	6	0.88	0.14
La	27	28	10	7	36	20	37	0.87	0.10
Ce	50	52	20	12	73	43	74	0.91	0.27
Nd	28	28	10	10	41	20	32	0.96	0.84
Eu	1.8	2	0.5	0.9	2	1	1	0.86	0.08
Tb	0.9	1	0.3	0.2	1	1	1	0.87	0.10
Tm	0.3	0.4	0.1	0.1	0.4	0.3	0.4	0.86	0.07
Yb	2.5	2	0.9	0.8	4	2	2	0.95	0.72
Hf	6.7	7	1.9	2.4	10	4	4	0.85	0.07
Та	1.1	1	0.5	0.2	2	1.5	1	0.88	0.13
Au	0.1	0.1	0.1	0.02	0.2	1	ND	0.87	0.09
Th	4.2	4	1.9	0.9	6	11	12	0.91	0.26
U	1.3	2	0.5	0.3	2	2.8	3	0.89	0.15

Shapiro-Wilk test for normality was applied to all determined elements. The results show 95 % probability ( $p \le 0.05$ ) that all elements were normally distributed, except Cl, Fe, Co, Zn, and Br. In cases where the probability was decreasing to 1 % (p < 0.01) for Cl, 4 % (p < 0.05) for Fe, 1 % (p < 0.01) for Co, 2 % (p < 0.02) for Zn, and 1 % (p < 0.01) for Br, Anderson-Darling normality test was applied and the same results were obtained.



Fig. 1. Boxplot of 36 major and trace elements in soil profile normalized to the corresponding values in the Upper Continental Crust [20]

Overall, the contribution of each investigated depth can be given as a fraction  $(C_{layer}/C_{total}) \cdot 100\%$ . The highest contribution from all the studied elements was observed for 0.25, 8, 3, 1, 0.5, 2, 4, 11, 10, and 17 with portions in percentage of 14, 13, 13, 13, 13, 13, 8, 8, 8, 6, and 3, respectively. It can be explained by the excess use of fertilizers and human impact on the surface soil. Contrariwise, the concentrations of the elements are decreased at high depths and most probably due to the undisturbed soil layers are still intact and there is no anthropogenic impact. Largely, the obtained results of the 1<sup>st</sup> investigated depth are in a good matching with the corresponding values for soils reported by Badawy et al. [22] in a dataset of the elemental composition of soil in Nile River and Delta.

#### Vertical distribution of thorium and uranium

Geochemically related elements are plotted in Figure 2 and the results in Table 1 show that the concentration of Th ranges from 0.9 to 6 mg/kg with a mean value of  $4.2 \pm 1.9$  mg/kg. The maximum values occurred at 1 to 3 m depth as in Figure 2a. The concentration of U ranges from 0.3 to 2 mg/kg with a mean value of  $1.3 \pm 0.5$  mg/kg. The maximum value was observed at 0.5 m depth. The obtained results were compared with corresponding values reported by Rudnick, Gao [20] and Viers et al. [21] and were generally lower. Further to that comparison, the Th/U ratio of 3.8 derived by Taylor and McLennan [23], 3.8 reported by Condie [24], 4.1 given by Wedepohl [25], and 3.9 based on the results reported by Rudnick and Gao [20] for UCC were compared to the ratio obtained in this present work of 3.2. Regardless the reduced concentration, the Th/U value is in a good agreement with the reported values above. Significant concentrations of U and Th at the upper layers and slight decrease with depth were noticed. This finding can be explained by the intensive use of fertilizers in the upper layers for agricultural purposes, which, in

turn, enhanced the accumulation of Th and U [26-28]. Karadeniz, Yaprak [28] found uniform distribution of U and Th within soil profile down to 50 cm depth.



Fig. 2. Distribution of the concentration of 7 groups of elements according to their similar behaviour within depth

### Vertical distribution of chloride and bromine

Chloride (Cl) and bromide (Br) ions are ubiquitous solutes in all natural water [29]. The first is a major component, the latter a minor one. The ocean has relatively uniform Cl and Br concentrations and the Cl/Br molar ratio is around 655  $\pm$ 4 [30]. The Cl/Br ratio has been used as a tracer to determine the origin and evolution of groundwater, surface water

and brines in oil and gas exploration and as a tracer to identify the origin of salinity in aquifers [30]. The Cl/Br ratio can be also employed to identify the groundwater flow system when salinity increases due to rock-water interaction and the results show a Cl/Br molar ratio of 116.6, which is significantly lower than the typical ratio (300-1500) for groundwater [30]. This ratio is lower than the generally reported values for ground water and silicate rocks. This means that the salinity of groundwater in the studied profile is not high and it may be attributed to the influence of Nile River. It is obvious from Figure 2c that the two elements have similar behaviour below 4 m depth.

### Vertical distribution of major elements

Figure 1 shows the mean, median, maximum and minimum values of the major elements. It is obvious that the normalized concentration of Mg, Ti and Ca is higher compared with the mean values reported for UCC [20]. While the concentrations of Na, Al and Ca are slightly lower in comparison with the mean UCC [20]. The behaviour of the six elements is almost the same as illustrated in Figure 2b. It is clear from the graph that these set of elements have maximum concentrations at 8 m depth and then decreased as the depth increased. Similar behaviour was observed in the case of Ti-V (Fig. 2d), Nb-La-Ce-Nd-Sm (Fig. 2e), Eu-Tb-Tm-Yb-Hf-Ta (Fig. 2f), and Mn-Zn-Rb-Sr-Zr (Fig. 2g).

#### Vertical distribution of trace elements

Table 1 presents the concentrations of some selected rare earth elements REE measured in the samples from the soil profile. The average concentrations of the REE vis., La, Ce, Nd, Eu, Tb, Tm, and Yb are compared with the corresponding values published by Rudnick, Gao [20] and Viers et al. [21].



Fig. 3. UCC-normalized distribution of REE patterns in soil profile samples (sample IDs are corresponding to their depths [m]). UCC normalizing values are from Rudnick and Gao [20]

The results of the comparison revealed that concentration of the REE are lower than those it compared with. The normalization of REE with respect to the corresponding values for UCC by Rudnick, Gao [20] shows that there are no enriched elements. It is clear from Figure 3 that the REE are slightly depleted except Eu, which is slightly enriched. Although it is typical for Eu but this finding is in good agreement with similar work done for stream and overbank sediments by Saydam Eker et al. [31].

#### Findings of the discriminant DA analysis and sedimentary provenance

Low mobility and incompatible elements viz., Sc, V, Cr, Ni, Zr, La, Hf, and Th can be used to get more information about the possible existence of natural volcanic origin materials in the analysed samples. It could be done by analysing the reciprocal distribution of these elements. Based on this fact, the ternary discriminatory diagram Sc-La-Th was plotted and compared with the corresponding elements reported by Rudnick, Gao [20], Viers et al. [21] and Savenko [32] as shown in Figure 4. The discriminatory diagram shows that the obtained data is a bit far from the corresponding values from the literature and tends to have a basalt and andesite origin and a slight tendency to felsic volcanic rock. This is attributed to the High Ethiopian Plateaus mainly consisting of basal with a small amount of felsic volcanic rocks [12, 33]. This result was confirmed by ratio indicators of La/Th and Th/Sc. These ratios are good indicators for provenance identification of elements. La/Th values range from a minimum value of 5.6 to a maximum value of 8.4 and Th/Sc ranges from 0.13 to 0.36. These values suggest mixed sources of basalt and andesite (7) for La/Th, and basalt (0.18) and andesite (0.48), respectively. The obtained results are in a good matching with the corresponding values of basalt and andesite.



Fig. 4. Ternary diagram shows the relation between Sc-La-Th compared with the corresponding elements reported by Rudnick and Gao [20], Viers et al. [21] and Savenko [32]. The figure shows that the origin of these elements tends to be mixture of basalt and andesite



Fig. 5. The Th/Sc vs Zr/Sc biplot illustrating a reduced degree of Zr enrichment, proving a low sediment recycling, a characteristic for majority of soil samples as data confirmed by Viers et al. [21], Gromet et al. [34] and Savenko [32]. The obtained results were proved in earlier work done by Badawy et al. [12] and Arafa et al. [2]

To extract information about the sedimentary provenance and identify the difference between felsic and mafic sources of materials, ratios of incompatible and compatible elements can be used. Figure 5 shows the Th/Sc vs Zr/Sc biplot illustrating a reduced degree of Zr enrichment, proving a low sediment recycling and low concentration of Th, a characteristic for majority of soil samples as data confirmed by Viers et al. [21], Gromet et al. [34] and Savenko [32]. The obtained results were proved in earlier work done by Badawy et al. [12], Arafa et al. [2]. This fact is another prove that most likely, the origin of elements is within the basalt and andesite region and slight tendency to felsic volcanic rock as in Th/Sc vs Zr/Sc biplot. Another evidence that the source of materials is basaltic and andesitic origin is the ratio of La/Sc and Co/Th. Clastic sedimentary rocks generally have La/Sc ratio ( $\approx$  1.5) of less than 2 and a Co/Th ratio ( $\approx$  6.9) concentrated between 1 and 10, and the samples are concentrated within basalt and andesite fields. These findings are in line with those published by Zhang et al. [35], Badawy et al. [12]. Additionally, it should be noted that the Th/Sc ratio is 0.2 which is close to the mafic source of materials according to Gu et al. [36].

#### Inter-correlation and the principal component PCA analysis

Looking at Table 2, it stipulates the correlation matrix of the obtained results of the elements (Pearson's method at p < 0.05). It is clear from the Table that Mg strongly correlates with Fe, Ti, V, Cr, Mn, Co, Zr, Nb, and Hf with a correlation coefficient greater than 0.95. The matrix of element correlation coefficients shows that aluminium in a good correlation with magnesium (r = 0.84), titanium (r = 0.84), and iron (r = 0.92), but weakly with sodium (r = 0.33) and calcium as well. These correlations could indicate the presence of biotite, and magnesium-rich alumino-silicates, a common occurrence in igneous and metamorphic rocks [2].

Principal component analysis PCA was performed considering all the samples that were collected from different depths. This analysis extracted four groups of elements as shown in Figure 6.

Out of 36 elements studied, 24 were related to factor 1, including rare-earth elements, several lighter transition metals (Mo and Sc), two halogens (Cl and Br) and the two actinides (U and Th). Factor 2 comprises mostly alkali and alkaline-earth metals, which, largely, participates in the internal circulation of the terrestrial ecosystem in the Nile Delta. These elements are to a considerable extent recirculated in the topsoil.



Fig. 6. Results of PCA of all 36 elements

Table 2

Correlation matrix of the obtained results of the elements (Pearson's method)

Element	Na	Mg	Al	Si	Cl	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Zn	As	Br	Rb
Mg	0.6																	
Al	0.3	0.8																
Si	0.1	0.1	0.0															
Cl	-0.3	0.3	0.6	-0.1														
Ca	0.9	0.8	0.5	0.1	-0.1													
Sc	0.2	0.9	0.9	-0.1	0.5	0.5												
Ti	0.8	0.9	0.8	0.2	0.2	0.9	0.8											
V	0.6	0.9	0.9	0.1	0.3	0.8	0.9	1.0										
Cr	0.7	0.9	0.7	0.0	0.2	0.9	0.8	0.9	0.9									
Mn	0.3	0.9	1.0	0.1	0.5	0.6	0.9	0.9	0.9	0.8								
Fe	0.3	0.9	0.9	-0.1	0.5	0.6	1.0	0.8	0.9	0.8	0.9							
Ni	-0.2	0.6	0.7	0.0	0.6	0.1	0.8	0.4	0.5	0.4	0.7	0.7						

Element	Na	Mo	A1	S	i	Cl	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Zn	As	Br	Rh
Co	0.5	00	0.8	2 _0	1	0.4	07	11			00	00	10	0.6	00	Lit	715	Di	no
7n	0.2	0.0	0.0		0	0.4	0.7	1.0			0.9	0.7	1.0	0.0	00				
	0.2	0.9	0.9		0	0.5	0.5	1.0		0.0	0.0	0.9	1.0	0.7	0.9	00			
As	-0.5	0.3	0.7		.0	0.7	0.0	0.0	0.3	0.3	0.4	0.7	0.8	0.8	0.0	0.8	0.0		
DI	-0.3	0.5	0.0	$\frac{-1}{2}$	.1	0.0	-0.2	0.		0.5	0.1	0.0	0.0	0.0	0.4	0.0	0.9	0.0	
Rb	0.1	0.8	0.9	<u> </u>	1.2	0.6	0.4	1.0	0.6	0.7	0.7	0.9	1.0	0.8	0.9	0.9	0.9	0.8	0.4
Sr	0.9	0.8	0.5	) -(	0.1	-0.1	1.0	0.3	0.8	0.7	0.9	0.6	0.6	0.0	0.7	0.5	0.0	-0.2	0.4
Zr	0.5	0.9	0.8	<i>s</i> –0	0.1	0.3	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.6	1.0	0.9	0.5	0.3	0.8
Nb	0.5	0.9	0.8	3 -0	0.2	0.5	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.5	0.9	0.9	0.5	0.4	0.9
Mo	-0.1	0.7	0.9	) -0	0.1	0.5	0.3	0.9	0.6	6 0.7	0.5	0.9	0.9	0.8	0.8	0.9	0.9	0.8	0.9
Ba	0.8	0.6	0.3	-0	0.2	-0.2	0.9	0.4	4 0.7	0.6	0.8	0.4	0.4	-0.1	0.6	0.3	-0.2	-0.3	0.3
Cs	-0.3	0.6	0.8	3 -0	0.1	0.7	0.1	0.9	0.4	0.5	0.4	0.8	0.8	0.9	0.7	0.8	1.0	0.9	0.9
La	0.0	0.8	0.9	-0	0.1	0.6	0.3	1.0	0.6	<i>0.7</i>	0.6	0.9	0.9	0.8	0.8	0.9	0.9	0.8	1.0
Ce	-0.1	0.7	0.8	3 -0	.1	0.6	0.3	0.9	0.6	6 0.7	0.6	0.9	0.9	0.8	0.8	0.9	0.9	0.8	1.0
Nd	0.3	0.8	0.8	8 0.	.0	0.5	0.6	0.9	0.8	8 0.8	0.8	0.9	0.9	0.7	0.9	0.8	0.6	0.5	0.9
Eu	0.1	0.8	0.8	3 -0	.3	0.5	0.3	0.8	8 0.6	<b>0.7</b>	0.5	0.8	0.8	0.8	0.7	0.8	0.7	0.7	0.9
Tb	0.0	0.8	0.9	) -0	).1	0.6	0.4	1.0	0.7	0.7	0.7	0.9	1.0	0.8	0.9	0.9	0.9	0.8	1.0
Tm	0.3	0.8	0.7	7 -0	.4	0.4	0.6	0.9	0.7	0.7	0.8	0.8	0.9	0.7	0.9	0.9	0.7	0.5	0.9
Yb	0.4	0.9	0.9	0	0	0.5	0.6	0.2	3 0.8	0.9	0.7	0.9	0.8	0.5	0.8	0.8	0.6	0.5	0.8
Hf	0.6	10	0.9	2 _0	1	0.3	0.8	0.0			10	0.9	0.0	0.5	10	0.0	0.5	0.3	0.8
Ta	0.0	0.0	0.0		0	0.5	0.0	1.		0.7	0.6	0.7	0.7	0.5	1.0	0.0	0.0	0.5	1.0
14	0.0	0.0	0.9		.0	0.0	0.5	1.0		0.7	0.0	0.9	0.9	0.0	0.0	0.9	0.9	0.0	1.0
Au	-0.4	0.5	0.5	7 -0		0.0	-0.1	0.0	$\frac{0.1}{0.1}$	0.5	0.1	0.5	0.0	0.0	0.4	0.0	0.0	0.9	0.7
	-0.5	0.0	0.7	$\frac{1}{2}$	0	0.0	0.1	0.5	0.4	0.3	0.5	0.8	0.8	0.8	0.7	0.8	1.0	0.9	0.9
U	0.0	0.7	0.8	<b>S</b> 0.	.0	0.6	0.3	0.9	0.6	0.7	0.7	0.9	0.9	0.8	0.8	0.9	0.9	0.8	0.9
Element	C.,	2	7	Mb	M		) a	$C_{\alpha}$	La	Ca	Md	E.,	Th	Tm	Vh	Пf	$T_{\alpha}$	A	Th
Element	Sr	Z	r	ND	IVIC		a	CS	La	Ce	Iva	Еи	10	1111	10	пј	14	Аи	In
Mg	_					_													
Al						_													
Si																			
Cl																			
Ca																			
Sc																			
Ti																			
V																			
Cr																			
Mn																			
Fe																			
Ni																			
Co																			
Zn	1		-+											1		1	1		
As	1		$\neg$		-									1		1	1		
Br	1		+		-									1		1	1		
Rh	1	+	-+										<u> </u>			-	1		
Cr.	+	-	-+		-								<u> </u>			+	+		
7.	0.0		$\dashv$			_										+	+		
	0.8		0			_											-		
Nb	0.8		.0	07		_								<u> </u>		<u> </u>			
Mo	0.2	0	./	0.7		_						L				<b> </b>			
Ва	1.0	0.	.7	0.7	0.0	)							L	ļ		<u> </u>	1		
Cs	0.1	0	.6	0.6	1.0	) _(	).1									ļ	1		
La	0.3	0.	.8	0.8	1.0	0 0	.1 .	1.0											
Ce	0.3	0.	.7	0.8	1.0	0 0	.1	1.0	1.0										
Nd	0.6	0.	.9	0.9	0.7	7 0	.4	9.7	0.8	0.8									
Eu	0.3	0	.7	0.7	0.9	0	.2 (	9.8	0.9	0.9	0.7								
Tb	0.4	0.	.8	0.8	1.0	0 0	.2 .	1.0	1.0	1.0	0.8	0.9		1					
Tm	0.6	0.	9	0.9	0.8	3 0	.6	0.7	0.8	0.8	0.8	0.8	0.9						
Yb	0.6	0.	.8	0.9	0.8	8 0	.4	).7	0.8	0.8	0.8	0.8	0.8	0.7		1	1		

			-		-	-	-	-	-	-			-	-			
Element	Sr	Zr	Nb	Mo	Ba	Cs	La	Ce	Nd	Eu	Tb	Тт	Yb	Hf	Та	Au	Th
Hf	0.8	1.0	1.0	0.7	0.7	0.6	0.8	0.7	0.9	0.7	0.8	0.9	0.8				
Та	0.3	0.8	0.8	1.0	0.1	1.0	1.0	1.0	0.8	0.9	1.0	0.8	0.8	0.7			
Au	-0.1	0.4	0.5	0.7	-0.2	0.8	0.8	0.8	0.6	0.7	0.7	0.6	0.4	0.3	0.7		
Th	0.1	0.6	0.6	0.9	-0.1	1.0	1.0	1.0	0.7	0.8	0.9	0.7	0.6	0.6	1.0	0.8	
U	0.3	0.8	0.8	0.9	0.1	0.9	1.0	0.9	0.8	0.7	0.9	0.7	0.7	0.7	0.9	0.7	0.9

Significant values are marked in italic bold

# Conclusion

The current study achieved its primary objective by reporting a comprehensive data on major and trace metals of 10 soil samples collected at 0.25-17 m depth. The epithermal neutron activation analysis was utilized. The distribution of 36 major and trace elements were discussed in terms of concentrations, geochemistry, and provenance within the soil profile. The normalized values of the elements show considerable concentrations of Mg, Cl, Ti, Zr, and rare earth elements REE. The log-distribution of the normalized REE show no anomalies, except for Eu. The discriminatory analysis shows that the provenance of the investigated samples is mostly a mixed source from clay, silt, sand, and gravel with a significant tendency to metabasic and andesite sources. Furthermore, it shows that the results of the ratio indicators of Th/Sc versus Zr/Sc show a reduced degree of Zr enrichment, proving a low sedimentary recycling. The principal component analysis PCA shows four groups of elements that have common geochemical treats. The ratio indicator of Th/U is 3.2 and a good matching with the corresponding values of UCC (4.7). The low Cl/Br ratio indicates the low salinity of the groundwater in the studied profile.

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### References

- Stanley JD. Nile delta: extreme case of sediment entrapment on a delta plain and consequent coastal land loss. Mar Geol. 1996;129(3):189-95. DOI: 10.1016/0025-3227(96)83344-5.
- [2] Arafa WM, Badawy WM, Fahmi NM, Ali K, Gad MS, Duliu OG, et al. Geochemistry of sediments and surface soils from the Nile Delta and lower Nile valley studied by epithermal neutron activation analysis. J Afr Earth Sci. 2015;107:57-64. DOI: 10.1016/j.jafrearsci.2015.04.004.
- [3] Stanley J-D. Egypt's Nile Delta in late 4000 years BP: Altered flood levels and sedimentation, with archaeological implications. J Coast Res. 2019;35(5):1036-50. DOI: 10.2112/JCOASTRES-D-19-00027.1.
- [4] Negm A. The Nile Delta. 1 ed. The Handbook of Environmental Chemistry 55. Cham: Springer International Publishing; 2017. ISBN: 9783319561240. DOI: 10.1007/978-3-319-56124-0.
- [5] Abd El-Ghani M, Huerta-Martínez FM, Hongyan L, Qureshi R. Human Impacts. In: Abd El-Ghani M, Huerta-Martínez FM, Hongyan L, Qureshi R, editors. Plant Responses to Hyperarid Desert Environments. Cham: Springer International Publishing; 2017. ISBN: 9783319591353. DOI: 10.1007/978-3-319-59135-3\_7.
- [6] Fishar MR. Nile Delta (Egypt). In: Finlayson CM, et al., editor. The Wetland Book: II: Distribution, Description, and Conservation. Dordrecht: Springer; 2018. ISBN: 9789400740013. DOI: 10.1007/978-94-007-4001-3\_216
- [7] Keshta AE, Shaltout KH, Baldwin AH, Sharaf El-Din AA. Sediment clays are trapping heavy metals in urban lakes: An indicator for severe industrial and agricultural influence on coastal wetlands at the Mediterranean coast of Egypt. Mar Pollut Bull. 2020;151:1-6. DOI: 10.1016/j.marpolbul.2019.110816.

- Hamza W. The Nile Estuary. In: Wangersky PJ, editor. Estuaries. Berlin, Heidelberg: Springer; 2006. ISBN: 978-3-540-00270-3. DOI: 10.1007/698\_5\_025.
- [9] Brown K, Lemon J. Fact Sheets Cations and Cation Exchange Capacity. 2016. http://soilquality.org.au/factsheets/cations-and-cec-tas.
- [10] Badawy W, Chepurchenko OY, El Samman H, Frontasyeva MV. Assessment of industrial contamination of agricultural soil adjacent to Sadat City, Egypt. Ecol Chem Eng S. 2016;23(2):297-310. DOI: 10.1515/eces-2016-0021.
- [11] Badawy WM, Ali K, El-Samman HM, Frontasyeva MV, Gundorina SF, Duliu OG. Instrumental neutron activation analysis of soil and sediment samples from Siwa Oasis, Egypt. Phys Part Nucl Lett. 2015;12(4):637-44. DOI: 10.1134/s154747711504007x.
- [12] Badawy WM, Ghanim EH, Duliu OG, El Samman H, Frontasyeva MV. Major and trace element distribution in soil and sediments from the Egyptian central Nile Valley. J Afr Earth Sci. 2017;131:53-61. DOI: 10.1016/j.jafrearsci.2017.03.029.
- [13] Kralj D, Romic D, Romic M, Cukrov N, Mlakar M, et al. Geochemistry of stream sediments within the reclaimed coastal floodplain as indicator of anthropogenic impact (River Neretva, Croatia). J Soils Sed. 2016;16(4):1150-67. DOI: 10.1007/s11368-015-1194-3.
- [14] El-Gamal AA. Egyptian Nile Delta Coastal Lagoons: Alteration and Subsequent Restoration. In: Finkl CW, Makowski C, editor. Coastal Wetlands: Alteration and Remediation. Cham: Springer International Publishing; 2017. ISBN: 9783319561790. DOI: 10.1007/978-3-319-56179-0\_13.
- [15] El-Sheekh M. River Nile Pollutants and Their Effect on Life Forms and Water Quality. In HJ Dumont, editor. The Nile: Origin, Environments, Limnology and Human Use. Dordrecht: Springer; 2009. ISBN: 9781402097263. DOI: 10.1007/978-1-4020-9726-3\_19.
- [16] Frontasyeva MV. Neutron activation analysis in the life sciences. Phys Part Nucl. 2011;42(2):332-78. DOI: 10.1134/S1063779611020043.
- [17] Pavlov SS, Dmitriev AY, Frontasyeva MV. Automation system for neutron activation analysis at the reactor IBR-2, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. J Radioanal Nucl Chem. 2016;309(1):27-38. DOI: 10.1007/s10967-016-4864-8.
- [18] Pavlov SS, Dmitriev AY, Chepurchenko IA, Frontasyeva MV. Automation system for measurement of gamma-ray spectra of induced activity for multi-element high volume neutron activation analysis at the reactor IBR-2 of Frank Laboratory of Neutron Physics at the joint institute for nuclear research. Phys Part Nucl Lett. 2014;11(6):737-42. DOI: 10.1134/S1547477114060107.
- [19] R Core Team. R: A language and environment for statistical computing. 2016. Vienna, Austria. R Foundation for Statistical Computing. URL: http://www.R-project.org/.
- [20] Rudnick RL, Gao S. 4.1 Composition of the Continental Crust A2 Holland, Heinrich D. In: Turekian KK, editor. Treatise on Geochemistry. Second Ed. Oxford: Elsevier; 2014. ISBN: 9780080983004. DOI: 10.1016/B978-0-08-095975-7.00301-6
- [21] Viers J, Dupre B, Gaillardet G. Chemical composition of suspended sediments in world rivers: New insights from a new database. Sci Total Environ. 2009;407(2):853-68. DOI: 10.1016/j.scitotenv.2008.09.053.
- [22] Badawy WM, Duliu OG, Frontasyeva MV, El-Samman H, Mamikhin SV. Dataset of elemental compositions and pollution indices of soil and sediments: Nile River and delta - Egypt. Data in Brief. 2020;28. DOI: 10.1016/j.dib.2019.105009.
- [23] Taylor SR, McLennan SM, The continental crust, its composition and evolution: an examination of the geochemical record preserved in sedimentary rocks. Oxford: Blackwell Scientific. 312. 1985. ISBN: 9780632011483.
- [24] Condie KC. Chemical-composition and evolution of the upper continental-crust contrasting results from surface samples and shales. Chem Geol. 1993;104(1-4):1-37. DOI: 10.1016/0009-2541(93)90140-E.
- [25] Wedepohl KH. The composition of the continental crust. Geochim Cosmochim Acta. 1995;59(7):1217-32. DOI: 10.1016/0016-7037(95)00038-2.
- [26] Uosif MAM, Mostafa AMA, Elsaman R, Moustafa E-S. Natural radioactivity levels and radiological hazards indices of chemical fertilizers commonly used in Upper Egypt. J Radiation Res Appl Sci. 2014;7(4):430-7. DOI: 10.1016/j.jrras.2014.07.006.
- [27] Ahmed NK, El-Arabi A-GM. Natural radioactivity in farm soil and phosphate fertilizer and its environmental implications in Qena governorate, Upper Egypt. J Environ Radioact. 2005;84(1):51-64. DOI: 10.1016/j.jenvrad.2005.04.007.
- [28] Karadeniz Ö, Yaprak G. Vertical distributions and gamma dose rates of <sup>40</sup>K, <sup>232</sup>Th, <sup>238</sup>U and <sup>137</sup>Cs in the selected forest soils in Izmir, Turkey. Radiat Prot Dosim. 2008;131(3):346-55. DOI: 10.1093/rpd/ncn185.
- [29] Alcalá FJ, Custodio E. Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal. J Hydrol. 2008;359(1-2):189-207. DOI: 10.1016/j.jhydrol.2008.06.028.

- [30] Davis SN, Whittemore DO, Fabryka-Martin J. Uses of chloride/bromide ratios in studies of potable water. Ground Water. 1998;36(2):338-50. DOI: 10.1111/j.1745-6584.1998.tb01099.x.
- [31] Saydam Eker Ç, Sipahi F, Gümüş MK, Özkan Ö. Tracing provenance and chemical weathering changes in Ankara Stream sediments, central Turkey: Geochemical and Sr-Nd-Pb-O isotopic evidence. J Afr Earth Sci. 2018;138:367-82. DOI: 10.1016/j.jafrearsci.2017.11.034.
- [32] Savenko SV. Geochemical aspects of biosedimentation. Dokl AN SSSR. 1986;288:1192-6.
- [33] GES. Geology of Ethiopia, Geological Survey of Ethiopia. 2016. http://www.gse.gov.et/.
- [34] Gromet LP, Haskin LA, Korotev RL, Dymek RF. The "North American shale composite": Its compilation, major and trace element characteristics. Geochim Cosmochim Acta. 1984;48(12):2469-82. DOI: 10.1016/0016-7037(84)90298-9.
- [35] Zhang X, Dalrymple RW, Yang S-Y, Lin C-M, Wang P. Provenance of Holocene sediments in the outer part of the Paleo-Qiantang River estuary, China. Mar Geol. 2015;366:1-15. DOI: 10.1016/j.margeo.2015.04.008.
- [36] Gu XX, Liu JM, Zheng MH, Tang JX, Qi L. Provenance and tectonic setting of the proterozoic turbidites in Hunan, South China: Geochemical evidence. J Sedimentary Res. 2002;72(3):393-407. DOI: 10.1306/081601720393.