XRF Analysis of Heavy Metals for Surface Soil of Qarun Lake and Wadi El Rayan in Faiyum, Egypt

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ABSTRACT

The environmental pollution with some heavy metals for twenty four surface soil samples collected from Qarun Lake and Wadi El Rayan region in Faiyum, Egypt utilizing X-ray fluorescence (XRF) spectroscopy was measured. The concentrations of 13 elements Cr, Ni, Cu, Zn, Zr, Rb, Y, Ba, Pb, Sr, Ga, V and Nb were determined. The elemental concentrations were compared with the normal values and other studies in different locations from the world. The correlation between elements appears that pollution inside the investigated lake and Wadi result from different sources of contamination present inside them. The results establish a database reference of radioactivity background levels around these regions.

Keywords: XRF; Heavy Metals; Surface Soil; Faiyum

1. Introduction

Studying the levels of radionuclide distribution in the environment provides essential radiological information [1-4]. As a result of rapid urbanization and industrial development, heavy metal contamination has been threatening human health [5]. A soil pollution assessment becomes very complex when different sources of contamination are present and their products are variably distributed. In these cases, the spatial variability of heavy metal concentrations in soils is basic information for identifying the possible sources of contamination and to delineate the strategies of site remediation.

The present study aims to assess the heavy metal contamination for surface soil of Qarun Lake and Wadi El Rayan regions in Faiyum, Egypt.

2. Material and Methods

Soil samples are collected from Qarun Lake and Wadi El Rayan in El Faiyum, middle Egypt, as shown in **Figure 1**. El Faiyum located 130 km southwest of Cairo. Qarun Lake is a closed saline lake, located in the deepest part of El Faiyum depression at the western desert, 70 km south Cairo-Egypt between longitudes 30°24' & 30°49'E and latitudes of 29°24' & 29°33'N. It has an area of about 200 km². It is used as a reservoir for the drainage water of El Faiyum province [6]. Qarun Lake water level is currently about 44 m below mean sea level [7]. The valley of Wadi El Rayan stretches on an area of 1759 km². About 65 km southwest of El Faiyum city and 80 km west of the Nile River. The reserve is composed of: A 50.90 km²-upper lake, 62.00 km²-lower lake, waterfalls between the two lakes. Wadi El Rayan waterfalls considered to be the largest waterfalls in Egypt. This region suffers from complex problems of pollution as a result of the high salinity in the water and presence of sewage, agricultural drainage flows inside it [8].

Twenty four surface soil samples, twelve from Qarun Lake (Q_1 to Q_{12}) and Twelve from Wadi El Rayan (W_1 to W_{12}), were collected from different locations along 12 kilometer, where the distance between each successive samples about one kilometer. The soil samples were dried, homogenized and sieved at 200 mesh grain size, pressed powder pellets were prepared by filling an alumina cup, (diameter 4 cm, height 1.2 cm and weight 3 gm), with 9 gm of crystalline boric acid covered by 1 gm of the grounded sample, and then pressed under 12 tons by using semi-automatic hydraulic press model HERZOG HTP-40. To avoid trace elements contaminations, the powdered samples were subjected to complete chemical analysis in the laboratories of Nuclear Materials Authority, Cairo

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Figure 1. Map of the geology of Faiyum indicating location of Qarun Lake, Wadi El-Rayan and the Faiyum depression, showing elevations in meters w.r.t. mean sea level.

Egypt, using the wet chemical analyses for the major oxides and XRD to analyze the trace elements.

Trace elemental analysis of samples by X-Ray fluorescence were performed using a Philips PW X-Unique II X-ray spectrometer with automatic sample changer PW 1510, (30 positions) at the Nuclear Materials Authority, Cairo, Egypt. This instrument is connected to a computer system using X-40 program for spectrometry. The trace elements concentrations are calculated from the program's calibration curves which were set up according to international reference materials, (standards), as NIM-G, G-2, GSP-1, AGV-1, JB-1 and NIM-D. The trace elements were measured by calibrating the system under the conditions of Rh-target tube, LiF-420 crystal, gas flow proportional counter, (GFPC), coarse collimators, vacuum, 30 kV and 40 mA for the determination of V, Cr, Co, Ni, Cu, Zn and Ga, 70 kV and 15 mA, for Rb, Sr, Y, Zr and Nb and 100 kV and 10 mA for the determination of Ba and Pb. The detection limit is the lowest concentration, and it is function of the level of background noise relative to an element signal [9]. The detection limit for the elements measured by XRF technique is estimated at 2 ppm for Rb, Nb, Ga, Co, Y and Sr and at 8 ppm for Pb and Cu and 5 ppm for other measured trace elements.

3. Results and Discussion

XRF results for collected surface soil samples from Qarun Lake and Wadi El Rayan regions evident the existence of the following elements: Cr, Ni, Cu, Zn, Zr, Rb, Y, Ba, Pb, Sr, Ga, V and Nb, shown in **Table 1**. It can be seen that Cr and Cu concentrations for all studied sites are greater than the normal values 30 and 20 mg/kg, respectively, while the Ni, Zn, Pb and V concentrations are lower than the normal values 20, 100, 20 and 50, respectively [10] for all studied sites except site Q_5 at Qarun Lake recorded high concentrations for Ni and V. It is

clear also that, samples have high concentration of Zr and Nb which means a presence of uranium and thorium in these samples. Also Sr has a great importance, since ⁹⁰Sr is a radioactive isotope with a half-life of 28.78 years. Table 1 also shows that, all samples contain a high concentration of Ba which can be separated using different methods in order to use it in different important industries [11]. Barium sulfate is important to the petroleum industry. Barium oxide is used in a coating of the electrodes of fluorescent lamps. Barium carbonate is used in glass-making. Barium fluoride is used for optics in infrared applications. Barium, commonly as barium nitrate, is used to give green colors in fireworks. Also, there are other trace elements like Rb, Y and Ga with different concentrations. A soil pollution assessment becomes very complex when different sources of contamination are present and their products are variably distributed [12].

Table 2 gives the comparison of trace element concentrations in present work with other reference data [10, 12-16]. It can be seen that the present concentrations of Cr, Ni, Cu, Zn and Pb is lower than that (ISIW) in Romania [10] and Hyderabad city in India [15] and all these concentrations exceeded threshold values [16]. **Table 2** shows also that the present concentration of V is lower than that of (ISIW) at Romania and the threshold value [16]. Existences of all these elements with different values caused many diseases if reached to human bodies [17]. For example, Cr caused carcinoma, Cu caused cirrhosis, nausea, vomiting and diarrhea, Ba high toxic substantive caused carcinoma, hypogonadism and diarrhea.

Using the elemental analysis data obtained (**Table 1**), we have calculated the matrices shown in **Tables 3** and **4**, by calculating the Pearson's correlation coefficient R^2 [18] between each two elements in soils collected from Qarun Lake and Wadi El Rayan, respectively.

From the correlation matrix of Qarun Lake (**Table 3**), it can be seen that the Pearson coefficient R^2 has greater values than 0.60 for the following pairs of elements: Ba-Pb, Ba-Rb, Ba-V, Ba-Ni, Cr-Nb, Cr-Sr, Cr-Y, Ni-Rb, Ni-Pb, Ni-V, Ni-Zn, Rb-Pb, Rb-V, V-Pb, Y-Sr, Zn-Ba, Zn-Pb, Zn-Rb and Zn-V. The correlation matrix of Wadi El Rayan samples (**Table 4**) shows that the Pearson coefficient R^2 has greater values than 0.60 for the following pairs of elements: Ba-V, Ba-Y, Ba-Zr, Zr-Cu, Zr-V and Zr-Y. This means that all elements that make an Rsquared value greater than 0.60 with another element will co-precipitate, to some extent, with that element. This relationship for a few selected elements in **Table 4**, proofs also that the pollution inside it is caused by different sources of contamination.

4. Conclusion

XRF technique has been employed in order to reveal their mineral composition to evaluate the pollution of soil

Sample	Cr	Ni	Cu	Zn	Zr	Rb	Y	Ba	Pb	Sr	Ga	V	Nb
Q1	98	12	43	44	79*	26	11	103	u.d	33	12	11	31
Q2	52	11	37	28	141	16^*	22	96	u.d	71	11	7^*	24
Q3	82	16	46	29	146	26	18	236	u.d	57	12	17	28
Q4	86	23	46	36	150	27	17	395	6	56	17^{**}	31	33**
Q5	62	46**	43	90**	168	51**	19	725**	17**	61	10^*	57**	28
Q6	48	17	46	27	146	16^*	22	153	u.d	70	11	15	22^*
Q7	26	9*	34*	32	152	17	26	57*	u.d	82	10^{*}	7^*	23
Q8	32	14	39	25^{*}	129	17	21	63	u.d*	67	11	7^*	24
Q9	29	13	37	32	166	19	26	166	4	84	10^{*}	14	23
Q10	34	12	35	28	149	17	34	144	u.d	75	11	11	24
Q11	44	23	43	49	231	39	27	529	6	85	10^{*}	40	25
Q12	56	15	40	37	182	27	26	302	u.d	80	11	21	25
W1	23*	18	52**	28	98	20	9*	155	u.d*	26	11	11	28
W2	203	15	48	33	252	22	24	285	2	69	11	12	27
W3	157	14	49	28	194	20	19	223	u.d*	59	12	12	28
W4	180	16	43	28	420	19	11	200	u.d*	34	12	14	30
W5	192	17	50	30	320	22	15	250	u.d*	100	11	14	29
W6	175	14	47	29	203	23	14	270	2	120	13	16	31
W7	160	17	46	32	554	24	35	302	2	17^{*}	12	16	28
W8	203**	15	49	27	168	18	16	193	u.d [*]	49	12	11	29
W9	145	15	48	31	118	25	11	251	u.d [*]	35	13	13	32
W10	194	14	48	32	260	20	20	291	$u.d^*$	78	12	15	31
W11	123	15	43	30	737**	21	38**	433	2	137**	11	17	27
W12	121	16	43	30	730	20	36	433	2	137**	12	17	30

Table 1. Trace elements concentrations (in ppm) using XRF spectroscopy for surface soil samples from Qarun Lake and Wadi El Rayan in Faiyum, Egypt.

*The lowest value; **The highest value.

Table 2. Comparison of the trace element concentrations (in ppm) for studied samples with other studies in different locations from the world.

Element	Karon Lake [*]	Wadi El Rayan [*]	Marmara Sea [12]	Gulf of Naples [13]	Saros Gulf [14]	(ISIW) at Romania [10]	Hyderabad, India [15]	Threshold value [16]
Cr	26 - 98	23 - 203	65 - 85	11 - 66	35 - 75	52.9 - 101.3	12.3 - 480.6	10 - 50
Ni	9 - 46	14 - 18	35 - 50	0.01 - 26.7	<5 - 75	41.9 - 65.6	12.6 - 132.0	10 - 50
Cu	34 - 46	43 - 52	20 - 80	3 - 664	<0.5 - 48	<15 - 52.8	11.1 - 186.6	10 - 40
Zn	25 - 90	27 - 33	60 - 145	77 - 1765	25 - 120	34.0 - 121.0	40.8 - 882.2	20 - 200
Zr	79 - 231	98 - 737						-
Rb	16 - 51	18 - 25						-
Y	11 - 34	9 - 38						-
Ba	57 - 725	155 - 433						100 - 1000
Pb	u.d - 17	u.d - 2				11.0 - 52.2	42.9 - 1832.5	10 - 30
Sr	33 - 85	17 - 137						-
Ga	10 - 17	11 - 13						-
V	7 - 57	11 - 17				95.5 - 110.7		30 - 150
Nb	22 - 33	27 - 32						-

*Present study.

Element	Cr	Ni	Cu	Zn	Zr	Rb	Y	Ba	Pb	Sr	Ga	V	Nb
Cr	1												
Ni	0.06	1											
Cu	0.52	0.21	1										
Zn	0.06	0.81^*	0.05	1									
Zr	0.17	0.12	0	0.06	1								
Rb	0.12	0.79^{*}	0.19	0.86^{*}	0.18	1							
Y	0.65^{*}	0.05	0.4	0.06	0.34	0.06	1						
Ba	0.06	0.85^{*}	0.22	0.72^{*}	0.35	0.89^{*}	0.01	1					
Pb	0.02	0.9^*	0.08	0.83^{*}	0.14	0.74^*	0.02	0.79^*	1				
Sr	0.73^{*}	0.02	0.28	0.04	0.57	0.03	0.74^*	0	0.002	1			
Ga	0.39	0.001	0.24	0.03	0.08	0.003	0.2	0.003	0.0003	0.25	1		
v	0.06	0.89^{*}	0.23	0.76^{*}	0.29	0.89^{*}	0.01	0.99^*	0.84^{*}	0.001	0.003	1	
Nb	0.78^{*}	0.13	0.33	0.12	0.09	0.21	0.49	0.14	0.11	0.59	0.57	0.15	1

Table 3. Correlation coefficent between trace elements in Qarun Lake, Egypt.

*Strong correlation.

Table 4. Correlation coefficent between trace elements in Wadi El Rayan, Egypt.

Element	Cr	Ni	Cu	Zn	Zr	Rb	Y	Ba	Pb	Sr	Ga	V	Nb
Cr	1												
Ni	0.28	1											
Cu	0.02	0.03	1										
Zn	0.07	0.01	0.02	1									
Zr	0.004	0.02	0.69^{*}	0.05	1								
Rb	0.001	0.001	0.002	0.37	0.001	1							
Y	0.0001	0.0004	0.37	0.19	0.74^*	0.008	1						
Ва	0	0.03	0.49	0.22	0.71^{*}	0.03	0.76^{*}	1					
Pb	0	0.01	0.29	0.20	0.38	0.12	0.56	0.53	1				
Sr	0.01	0.12	0.17	0.01	0.26	0.004	0.21	0.54	0.25	1			
Ga	0.05	0.23	0.03	0.01	0.05	0.12	0.06	0.01	0.002	0.01	1		
v	0.002	0.01	0.56	0.12	0.64^{*}	0.08	0.44	0.67^{*}	0.41	0.39	0.03	1	
Nb	0.03	0.09	0.004	0.0004	0.07	0.04	0.18	0.01	0.09	0.0004	0.64^*	0.03	1

*Strong correlation.

with heavy metals. The concentrations of thirteen elements (Cr, Ni, Cu, Zn, Zr, Rb, Y, Ba, Pb, Sr, Ga, V and Nb) in Qarun Lake and Wadi El Rayan regions were determined. A soil pollution assessment becomes very complex when different sources of contamination are present and their products are variably distributed with time assembling and become toxic. As a result of existent of all these elements, these places are pollutant and when using it in agriculture will cause danger to humans, since toxic substances will move toxic substances from soil into plants and then to human bodies. Therefore, we recommend not use it in agriculture, until solving the main problems of pollution in this region, such as high salinity in water and presence of sewage, agricultural drainage flows inside it and others. The results of this study can be used as a data baseline for preparing a radiological map of the study area, especially at the chosen sites.

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