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Determination of Uranium, Thorium, $^{238}U/^{232}Th$ Activity Ratio and Rare Earth Elements Distribution Using Neutron Activation Analysis (NAA)

[1,3] Nassef MH* and [2,3]Nawal M. Said#

[1]King Abdulaziz University, Faculty of Engineering, Nuclear Engineering Department, P.O. Box.80204, Jeddah 21589, Saudi Arabia
[2]El-Taif University, Faculty of Science, Physics Department, Saudi Arabia.
[3]Nuclear and Radiological Regulatory Authority, (NRRA) Cairo, Egypt.
#On leave from NRRA-Egypt
*Corresponding Author: M.H. Nassef Tel.: +508871229; fax+6952648

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ABSTRACT

In this study, uranium, thorium, cesium concentration and rare earth elements distribution pattern in addition to $^{238}U/^{232}Th$ activity ratio were determined in 27 collected environmental samples. The samples were analyzed using two different techniques: destructive technique such as neutron activation analysis (NAA) and non-destructive technique such as gamma-ray spectrometry. Concentrations of six rare earth elements were measured using NAA namely: Lu, Ce, Eu, Tb, Yb, and La. The sampling area has different locations across the whole eastern border of Egypt. For NAA technique, the samples were irradiated with neutrons using epithermal neutrons at the Joint Institute of Nuclear Research, Dubna, (Russia). The radioactivity assay was carried out using high-resolution gamma-ray spectrometry. The average concentration in the analyzed samples for ^{238}U, ^{232}Th, and ^{137}Cs was found to be 3.5, 3.93, and 0.83 ppm respectively. The measured values found within the average world range 2.8 (0.81-4.0), 8.6 (1.7-12.3) for ^{238}U and ^{232}Th respectively. The rare earth distribution pattern was determined for the analyzed samples. This distribution pattern is a characteristic signature for the studied area. The area monitored represents a database for any future radiological emergency action outside the country. Also, the obtained results can be used as a useful information data bank for the suggested national nuclear forensic database library and in a nuclear security application.

Keywords Neutron activation analysis. Nuclear forensics, wide area sampling

INTRODUCTION

One of the main activities of the International Atomic Energy Agency (IAEA) is to prevent turning any nuclear material especially fissionable

material from using in any undeclared process such as nuclear weapons devices.

The IAEA inspection measures such as accountancy of nuclear materials, containment, and surveillance, in-situ non-destructive measurements, a collection of environmental samples have been performed to confirm the declared activities for any nuclear facility (Zsuzsanna, 2012). Analysis of environmental samples is one of the important measures introduced in 1996 by IAEA. Nuclear activities, like any other industrial activity, release small amounts of their products into the environment. The material, which has been released, carries information on the process it arises from. Therefore, these nuclear signatures supposed to be characteristic of the process from which they originated (Buchmann at al., 2003; U.S. Congress, 1995). The concept of Wide-Area Environmental Sampling (WAES) was found effective in the field of inspection activities (Kukn et al., 2001; David et al., 2001; STUK, 2016). The IAEA defines the WAES as the process of collecting and analyzing any environmental samples such as (soil, vegetation, water, air, and smears) at specified locations. During the WAES program, the collection of any environmental samples can be done such as water, soil, and vegetation from or near the nuclear power facility grounds. But inside the nuclear facility, the swipes samples is recommended to take the samples in and near the process building. Some environmental samples such as vegetation showed traces of enrichment activities after analyzing those samples. The particle analysis of the swipe samples showed varies levels of uranium enrichment level starting from depleted, natural, low and high enriched uranium concentration. The advantage of applying swipe sample protocol is for comparison between all nuclear process inside and outside the building (U.S. Congress, 1995). The WAES strategy can extend too much larger areas up to hundreds of thousands of square kilometer. In addition, there are other information sources that are useful to the agency including open source analysis, satellite imagery, the existing agency safeguards inspections process, and the information collected from the member states (Kuhn et al., 2001; David et al., 2001; STUK, 2016; Pointurier et al., 2008; CNSC, 2013). For the marine environment, the IAEA recently start to analyze in detail the area of worldwide marine radioactivity as an advanced study due to its strategic interest. These strategic information for that areas may contain important information of the man-made radionuclides in the world's oceans and seas and that coming from the nuclear weapons testing, reprocessing of nuclear materials, nuclear waste, nuclear accidents, and the industrial or medical radioisotopes, whose distributions change based on geochemical, oceanographic, and biological processes (David et al., 2001). The environmental monitoring is useful to understand the cause and hazards of any radiological or nuclear accident such as what happened in Fukushima accident. A large amount of anthropogenic fallout of ^{137}Cs was deposited on the surface soils of Fukushima area during that accident. ^{137}Cs has a relatively long half-life of 30.2 years which is considered as one of the most significant radionuclides in environmental monitoring. Soil is the main source of fallout radionuclides such as ^{137}Cs and its migration behavior and associated profile distribution are site-specific and depend on the characteristics and the environmental conditions of the soil as in case of the analysis of Chernobyl accident (Mishra et al., 2014; Aya et al., 2012; David et al., 1994; Watanabe et al., 2012; THPS, 1994). The collection of environmental sampling such as vegetation, soil, and water outside the site of the nuclear facility is useful in the field of nuclear security and safety especially for radiological emergencies inside and outside any country in addition to its improvement for agency inspection activities (Kuhn et al., 2001; Shahabuddin et al., 2010). The concept of nuclear forensic science is defined as the interpretation to evaluate the analytical results from a collected sample using a set of authorized "signatures," so as to provide technical conclusions to the analyzer. The rare earth element (REE) distributions pattern in ore sample depends on its geologic conditions and the deposit type from which the ore formed. This distribution pattern represents a useful tool for the so-called nuclear forensic analysis (Jeong et al., 2016; Tyler et al., 2017). In this study, uranium, thorium concentrations, $^{238}U/^{232}Th$ activity ratio, and determination of rare earth concentration pattern in the collected samples was determined.

A total of 27 representative environmental samples collected and analyzed using a destructive technique such as neutron activation analysis (NAA) and gamma-ray spectrometry (nondestructive technique). The rare earth distribution pattern was determined for nuclear forensics and nuclear security purposes as a marker because these elements can be represented as characteristic fingerprints of soil in the studied area.

MATERIALS AND METHODS

Sample collection, preparation, and irradiation by NAA for determination of actinides

Twenty-seven soil samples were collected across the east border of Sinai-Egypt/from a selected region in Sinai-Egypt to be analyzed by Neutron Activation analysis (NAA) technique. About 0.2g from the samples heat-sealed in polyethylene foil bags for short-term irradiation and packed in aluminum cups for long-term irradiation in the pulsed fast reactor IBR-2M of Dubna (Russia). The IBR-2M pulsed research reactor has a power of 2MW. It generates a power pulse of about 1830 MW of 200μs duration with a frequency of 5Hz (Ananiev et al., 2012). Table 1 shows the neutron flux density characteristics in the irradiation channel equipped with the pneumatic system used in the analysis. The temperature in the irradiation channel was 70 ^{0}C. The samples irradiated for four days to determine uranium and thorium elements. After four to five days of decay, the samples were repacked and then measured. The relatively resonance cross-sections of uranium and thorium; 284 and 84 barns respectively, enable their determination with good precision. The free of interference gamma lines such as106.12 keV and 312.01 keV used for uranium and thorium determination.

Following activation, both the sample and standard were measured twice, after four days during 45 min and after 14 days for 1.5 h. For each sample, the gamma spectrum was measured using a Ge (Li) detector with an energy resolution of 2.2keV for the energy line of 1332.4keV for ^{60}Co and a total efficiency of 18%. For irradiated samples, the gamma emissions were measured by a hyper-pure germanium detector, which has a resolving power of 1.95keV at 1332.5keV energy line of ^{60}Co. during the measurements, the optimum conditions (e.g. measuring time, distance from the detector and the sample mass) were chosen to get the best results. The samples and standards were irradiated and counted under the identical condition and the same geometry. The total concentration of thorium was determined through detection of ^{233}Pa which produced from the neutron irradiation of ^{232}Th target nuclide. The concentration of uranium was determined through the detection of ^{239}Np with a gamma transition as shown in Table2.

Table1. The neutron flux density characteristics applied in the irradiation channel

Irradiation Channel	$\Phi_{th}\times 10^{12}$ (n/cm^2 s)				Channel	
	E = 0-0.55 eV Thermal	**E = 0.55-10^5 eV** Resonance	**E = 0.1-25 MeV** Fast	**t(^{0}C)**	diameter (mm)	length (mm)
Channel l	**0.023**	**3.31**	**4.32**	**70**	**28**	**260**
Channel 2	**1.23**	**2.96**	**4.10**	**60**	**28**	**260**

Table 2. The main gamma transitions produced from ^{238}U and ^{232}Th irradiation

Element	Produced Isotope	Energy (keV)	Intensity (%)
^{238}U	**^{239}Np**	**106.12**	**22.86**
		228.12	**10.79**
		277.60	**14.20**
^{232}Th	**^{233}Pa**	**300.18**	**6.20**
		312.01	**36.00**
		340.95	**4.00**

RESULTS AND DISCUSSION

The results of the neutron activation analysis of the samples are given in Table 3. From the distribution concentration of ^{238}U and ^{232}Th in the investigated samples, it was found that the uranium concentration ranged from 1.03 to 10.34 ppm with an average value of 3.5 ppm. Uranium found as a natural part from the total soil radionuclides component originating from rocks in the earth's crust. The basic rocks (basalts) contain up to 8 ppm; and sedimentary rocks (shale) contain, on average, 4 ppm of uranium as shown in Table 4. Table 4 shows different sources for uranium concentration in different matrices including soil and

the worldwide value. Table 4 shows the worldwide uranium concentrations in soil ranged from 0.81-4.0ppm with an average value of 2.8 ppm. Another study shows that the worldwide uranium concentration in soil reported in the range from 0.3 to 11.7 ppm. The uranium average concentration in the earth's crust ranges from 3 to 4 ppm as shown in

Table 4. Based on the above-mentioned results in Table 4, it seems that the measured average uranium concentration in the analyzed samples was found to be within the average world range distribution value in the soil. Table 3 shows that the thorium concentration in the same analyzing samples ranged from 1.81 to 8.07 ppm with an average value of 3.93 ppm. The soil contains thorium and its value normally increase with an increase in its clay content. In most soil, thorium will remain strongly sorbs into the soil and its mobility will be very slow. The typical concentration range of thorium in soil ranged from 2ppm to 12ppm, with an average value of 6ppm (Saiful et al., 2016). Table 4 shows that the worldwide thorium concentrations in soil ranged from 1.7 to 12.3ppm with an average value of 12.3ppm. The thorium concentration in the analyzed samples was found lower than the average world range distribution value in the soil. Figure 1 shows the variation in the measured average uranium, thorium and cesium-137 concentration for all the analyzed samples. No correlation was found between uranium and thorium concentration in the measured analyzed samples as shown in Figure 2.

Table 3. Uranium, thorium, cesium concentration values in ppm and the value of $^{283}U/^{232}Th$ ratio in the analyzed samples

Site No.	^{232}Th	^{238}U	$^{283}U/^{232}Th$ Ratio	^{137}Cs
1	2.93	1.15	0.39	0.30
2	2.73	1.18	0.43	0.16
3	3.24	2.52	0.78	1.01
4	2.46	1.03	0.42	0.30
5	2.79	5.25	1.89	0.88
6	3.31	3.35	1.01	1.27
7	2.14	1.16	0.54	0.61
8	5.08	1.82	0.36	1.30
9	2.25	4.39	1.95	0.52
10	1.81	1.29	0.71	0.41
11	3.01	2.16	0.72	0.86
12	3.52	2.70	0.77	0.82
13	2.38	1.91	0.80	0.38
14	3.72	2.54	0.68	0.89
15	4.02	2.03	0.51	0.57
16	2.94	7.53	2.56	1.08
17	2.50	4.45	1.78	0.38
18	8.07	3.10	0.38	1.22
19	3.30	3.45	1.05	0.62
20	7.65	3.17	0.41	1.41
21	6.22	3.48	0.56	1.17
22	4.83	3.71	0.77	1.06
23	6.40	3.41	0.53	1.50
24	3.19	9.07	2.84	0.59
25	5.92	3.34	0.56	1.07
26	2.37	10.34	4.36	0.72
27	7.23	5.06	0.70	1.27
Avg.value	3.93	3.50	1.05	0.83

1ppm U =12.4Bq/kg; 1ppm Th =4.06 Bq/kg.

Table 4. Typical uranium and thorium concentration levels in soil

Radionuclide concentration levels	Concentration in ppm	References
Uranium average concentration in the earth's crust	3 - 4	(Stokinger et al., 1999; NCRP, 1999; Riley et al., 1983; Berlin et al., 1979; Statistics Canada, 1983)
Worldwide uranium concentrations in soil	0.3 to 11.7 2.8 (0.81-4.0)	(UNSCEAR, 1993; Benedict et al., 1981; UNSCEAR, 2000)
Uranium concentration in rock	4-8	(Benedict at al., 198)
Uranium concentration in sedimentary rock	2-4	
Uranium concentration in sea water	0.003	
Worldwide thorium concentrations in soil	8.6(1.7-12.3)	(UNSCEAR, 2000)

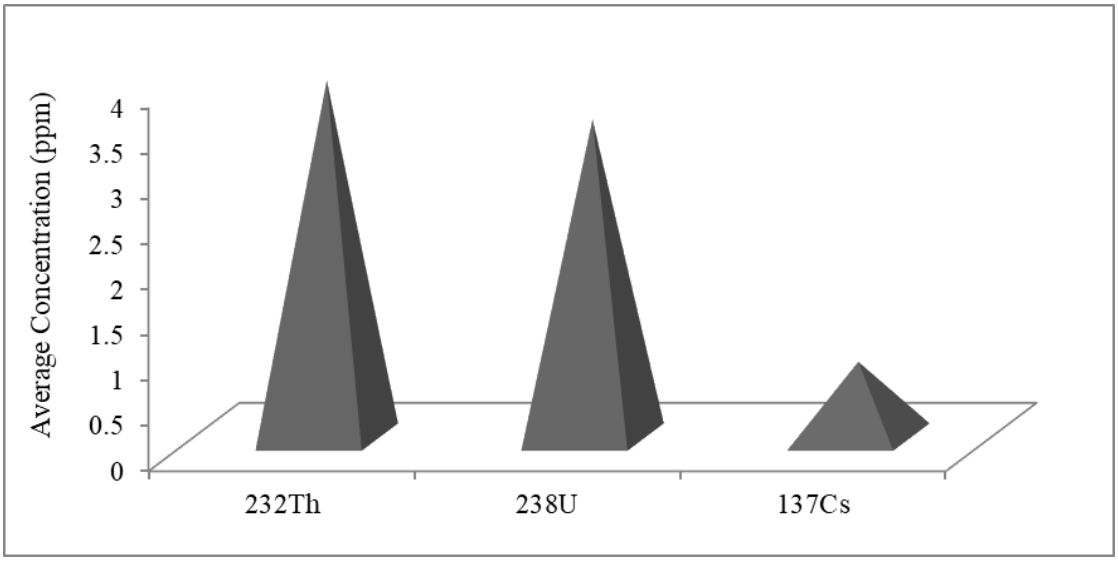

Fig. (1) Measured average concentration of ^{238}U, ^{232}Th, and ^{137}Cs in the analyzed samples

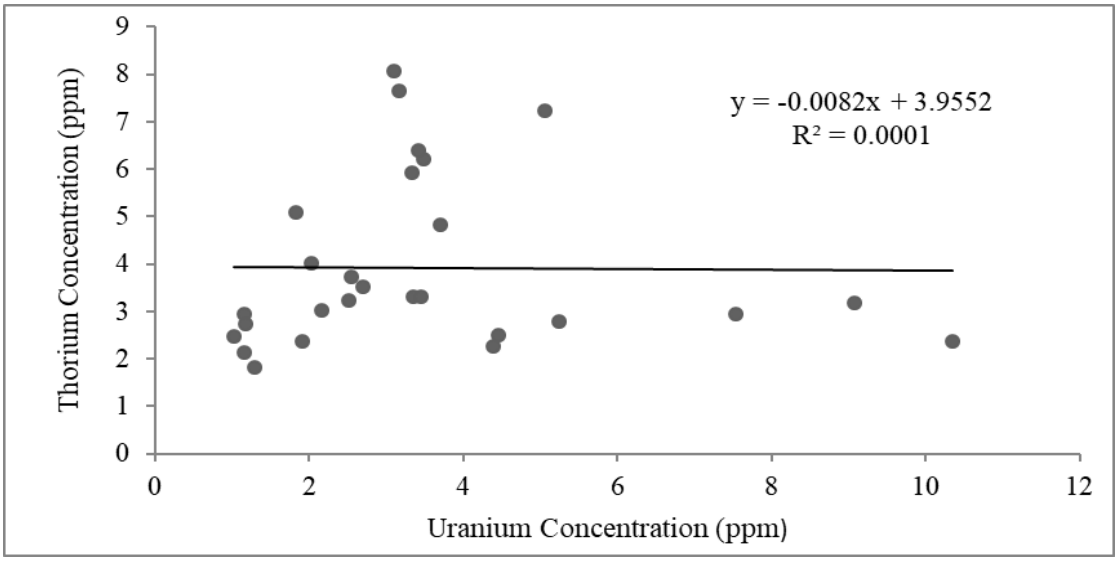

Fig. (2) Relationship between ^{238}U and ^{232}Th ratio in the analyzed samples

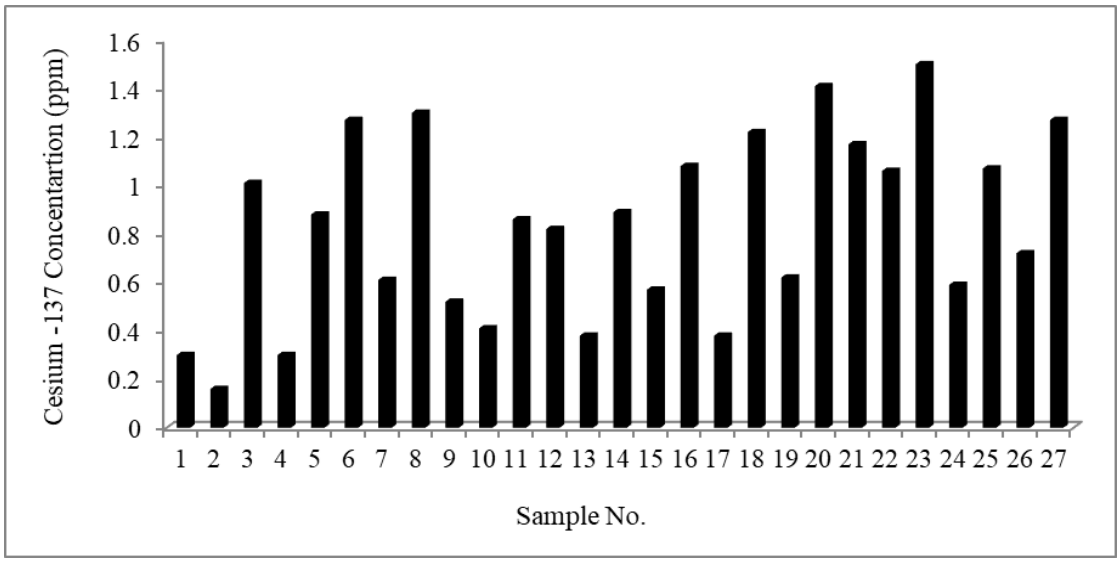

Fig. (3) Measured ^{137}Cs concentration in the analyzed samples

Table 5. Rare earth concentration level in ppm in the analyzed samples

Site No.	REE Concentration (ppm)					
	La	Ce	Eu	Tb	Yb	Lu
1	7.80	19.27	0.26	0.31	1.09	0.12
2	8.77	22.67	0.33	0.31	1.28	0.12
3	13.39	27.77	0.47	0.39	1.06	0.27
4	7.48	16.04	0.22	0.19	0.80	0.10
5	14.34	24.85	0.30	0.37	1.14	0.52
6	14.91	31.45	0.34	0.42	1.37	0.34
7	10.83	19.87	0.29	0.27	0.78	0.12
8	15.97	41.51	0.29	0.44	1.52	0.19
9	7.77	16.83	0.22	0.24	0.79	0.42
10	8.22	16.14	0.17	0.21	0.41	0.11
11	14.90	23.28	0.33	0.52	1.43	0.20
12	12.20	27.45	0.25	0.39	0.55	0.25
13	9.13	19.09	0.24	0.28	0.91	0.17
14	12.35	30.73	0.37	0.39	1.32	0.25
15	12.50	26.02	0.27	0.37	1.31	0.20
16	12.50	26.19	0.24	0.40	0.67	0.74
17	14.98	17.38	0.25	0.34	0.91	6.13
18	25.36	52.89	0.35	0.59	1.73	4.50
19	12.83	23.14	0.19	0.30	0.87	5.26
20	25.61	52.13	0.34	0.67	1.78	4.63
21	27.19	39.68	0.37	0.56	1.41	5.28
22	19.68	37.04	0.37	0.52	1.41	5.33
23	23.91	46.70	0.35	0.52	1.52	4.99
24	14.74	21.60	0.22	0.33	0.92	12.73
25	21.18	37.71	0.19	0.56	1.38	4.86
26	15.28	19.44	0.28	0.33	0.78	13.41
27	29.91	65.09	0.44	0.71	1.94	7.02

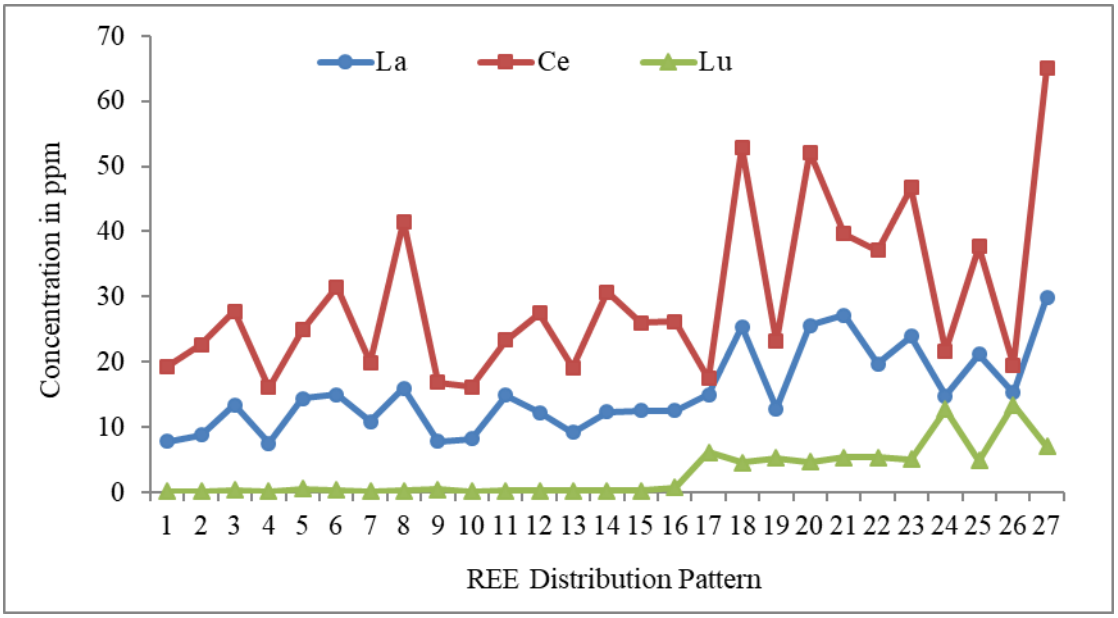

Fig. (4) Rare earth (La, Ce, and Lu) distribution pattern for the analyzed samples

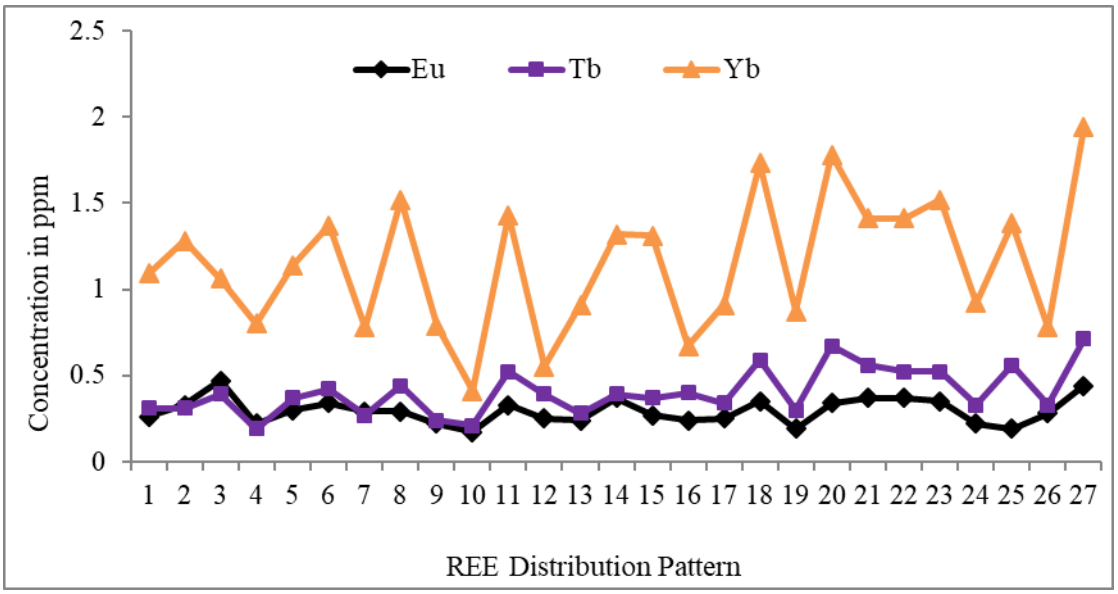

Fig. (5) Rare earth (Eu, Tb, and Yb) distribution pattern for the analyzed samples

The man-made ^{137}Cs concentration which released from nuclear testing, or from the nuclear accidents of any nuclear power or research reactor were given in Table 3. The ^{137}Cs concentrations in the analyzed samples ranged from 0.3 to 1.5ppm with an average value of 0.83ppm. The results show that there is no large variation in the measured value for cesium level in the analyzed samples. It is likely that precipitation amounts were closely related to ^{137}Cs concentrations in surface soil because ^{137}Cs in surface soil was deposited by wet and dry depositions and they tightly adsorb on the soil surface. Figure 3 shows the variation in the measured concentration of cesium in the analyzed samples.

The rear earth concentration in the analyzed samples was determined as a characteristic pattern for the studied area. For Lanthanum chemical element the concentration ranged from 7.8 ppm to 29.91ppm with an average value of 15.32ppm. For cerium, the concentration ranged from 16.04 ppm to 65.09ppm with an average value of 29.70 ppm. The concentration of europium in the analyzed samples ranged from 0.17 ppm to 0.47 ppm with an average value of 0.29ppm.

Terbium ranged from 0.19 ppm to 0.71 ppm with an average value of 0.31ppm. The concentration of ytterbium ranged from 0.41ppm to1.94 ppm with an average value of 1.15ppm. Finally, lutetium concentration ranged from 0.10 ppm to 13.41ppm with an average value of 2.89ppm. Figures 4&5 show the rare earth distribution pattern for the analyzed samples.

CONCLUSION

The rare earth distribution pattern was determined for the analyzed samples. This distribution pattern is a characteristic signature for the studied area. The measured values found within the average world range 2.8 (0.81-4.0), 8.6 (1.7-12.3) for ^{238}U and ^{232}Th respectively. Soil samples are an important source of environmental samples, which are selected for the monitoring of global fallout from any nuclear power plants or reactors in wide area monitoring. The area monitored represents a database for any future nuclear emergency accident outside the country. The obtained results can be used as a useful information data bank for the suggested national nuclear forensic database library and nuclear security field.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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