



Distribution and Bioaccumulation of Uranium and Thorium in Natural Soil and Wild Plants of Wadi El-Missikat, Central Eastern Desert, Egypt

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Uranium and thorium concentrations were determined in soil and wild plant samples collected from Wadi El Missikat, Central Eastern Desert, Egypt. The U and Th contents are similar to those in Gebel Qattar soil (North Eastern Desert, Egypt), but higher than their corresponding levels in the Earth's crust. The results obtained indicate that the *Fagonia boveana* plant uptakes and accumulates both elements, but uptakes of Th is higher than U. *Fagonia* sp. can absorb and accumulate uranium element with 150 times more than the average of world plant uptake. The *Zilla spinosa* plant was also found to be hyper-accumulator for U and Th and can absorb and accumulate uranium with 48 times more than the average world plant. Analyses of the studied plants show that they are considered hyper-accumulators for uranium and thorium and could be used as candidates for exploration for these elements and phytoremediation of radionuclide-contaminated soils.

Keywords: Uranium, Thorium, Wadi El-Missikat, Natural Wild Plants, Egypt

Introduction

Naturally occurring radioelements are generally present in soils and plants, but their contents in plants are in most cases very low. Nevertheless, ores of some sites show elevated levels of uranium and thorium [1, 2]. Radionuclide behavior in soils and bedrock with emphasis on uranium and thorium is very important issue from an environmental point of view [3]. In spite of numerous publications about mobilization of uranium and thorium from soil to plants, studies on the absorption of thorium are rare [4, 5]. Several investigations have been published on the biogeochemistry of thorium [6, 7, 8]. Sharma et al. [9] mentioned that phytoremediation is one of the most promising techniques for a large scale treatment of radionuclide contaminated soils.

A food-chain model is necessary for estimating human doses in regard to plant uptake from soils where there is any question of impact by a contaminant in the geosphere. Accordingly, the

transfer factor (TF) or distribution coefficient from the soil to the plant must be quantified [10]. The transfer factor (TF) is the ratio between the concentration of radionuclide in the plant to that in the soil [11].

Some of the younger granites in the Eastern Desert of Egypt have been found to host significant uranium mineralization [12, 13]. The uranium mineralization in Qattar, El-Missikat (study area) and El-Erediya plutons is structurally controlled and restricted to shear zones where uranium bearing minerals occur either as small veinlets or as minute dissemination associated with hydrothermal alteration. Hussein and Sayyah [12] estimated as much as 8000 tons of uranium metal as speculative resources in the El-Missikat and El-Erediya occurrences. Gebel El-Missikat granites represent one of the most promising examples of the fracture-filling uranium occurrences in the Central Eastern Desert of Egypt. Wadi El-Missikat

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lies in the Gebel El-Missikat area and collects flood sediment from the internal tributaries along El-Missikat granites and other rock types. Radiation hazard and risks due to natural radioactivity in some Egyptian ores and soils are given in recent publications [2, 13].

Zilla spinosa and *Fagonia boveana* (the studied species) in Qattar area, North Eastern Desert, Egypt can concentrate and accumulate several heavy and rare elements such as, Pb, Mo, Co, Ni, Sr, Cu, Zr, Cd, As, Ag, Sb, Bi, V, Cr, Cs, Bi and Se of concentrations exceeding the world plant average WPA [14, 15]. *Aerva Javanica* plants collected from the area near Allaqi gold mine in Aswan, South Eastern Desert, can uptake and concentrate some trace elements such as Ag, As, Cd, Co, Cr, Mo and Ni of concentrations exceeding WPA [16].

Wadi El-Missikat contains different species of wild plants. Most of these species are considered ephemeral plants and some as grazing plants. Two species, *zilla spinosa* and *fagonia boveana* are perennial plants. Landsat image of the El-Missikat area shows sample locations of the studied soil and plants in Wadi El-Missikat (Fig. 1).

The primary objective of the present study is to determine ^{238}U and ^{232}Th concentrations in environmental samples of soil and plants collected from Wadi El-Missikat to assist with assessing environmental radiological impacts in the future.



Fig. (1): Landsat image showing sample location of the studied soil and plants in Wadi El Missikat and landsat image of El Missikat area

Material and Methods

Plant sampling and study

Plant samples were collected at blooming duration for determination of radio elements accumulation. The studied plant species are: *Zilla spinosa* Fig. (2) and *Fagonia boveana* Fig. (3) of Brassicaceae and Zygothyllaceae families, respectively.

All collected samples of plant were packed in paper bags to prevent cross contamination and shipped to the laboratory. In the laboratory, plant samples were gently washed with deionized distilled water for 2 min to remove the soils adhered and then the plant and soil samples were kept for drying at room temperature. Then the concentrations of U and Th in plant samples were determined using inductively coupled plasma / Emission spectrography and Mass spectrometry (ICP-ES and MS).



Fig. (2): *Zilla spinosa* plant



Fig. (3): *Fagonia boveana* plant

Plant analysis

Dried plant samples were analysed by adding 2 mL of concentrated nitric acid for an hour and then a solution consisting of 2 ml Hydrochloric acid + 2 ml Nitric acid + 2 ml hydrogen peroxide at 90°C for one hour. The solution was then diluted to 20 ml, and analysed by ICP/ ES & MS techniques to determine ^{238}U and ^{232}Th elements [17].

Soil analysis

Soil samples were taken from the zone under the selected plants (the root zone) at a depth interval of 40 cm by digging profiles. The soil samples were prepared by an alkali fusion method [18] and then analysed and measured to determine the radioactive elements using the ICP-ES and MS technique. Chemical analysis of plant and soil samples was carried out at ACME analytical Laboratories of Vancouver, Canada. Detection limits for trace elements were 0.01–0.5 ppm. The analytical precision, as calculated from replicate analyses varied from 2% to 20% for trace elements.

Transfer factor (TF) for plants

The potential of a plant to be used in phytoremediation does not merely depend on the concentration of the element in the plant; it also depends on the transfer and the accumulation ability for the target element [19].

Some plant species have developed tolerances towards elements. Others (hyper-accumulators) are characterised by their ability to accumulate large quantities of elements in their tissues [20]. Hyper-accumulators are plants that achieve a plant-to-soil elements-concentration ratio (transfer factor) of greater than one. The accumulation of these elements may vary from plant to plant and soil to soil. If these factors are constant, the uptake of elements by different plant species may be compared.

Ratio or transfer factor (TF) is calculated to determine the extent to which elements accumulate in the plants according to the following formula [16, 21]:

$$\text{TF} = \frac{\text{Concentration of elements in plant}}{\text{Concentration of elements in soil}}$$

Ratio of concentration values or TF may vary over several orders of magnitude, depending on the soil and plant species [22]. It is assumed in the TF

calculation that there is a linear relationship between total soil uranium concentration and plant tissue concentration [22].

Values of eU and eTh in ppm were converted to activity concentration, in Bq kg^{-1} , using the conversion factors given by the International Atomic Energy Agency [23] and by the Polish Central Laboratory for Radiological Protection, as shown in [24]. The specific parent activity of a sample containing 1 mg kg^{-1} , by weight, of ^{238}U is 12.35 Bq kg^{-1} and 1 mg kg^{-1} of ^{232}Th is 4.06 Bq kg^{-1} .

Both ^{238}U and ^{232}Th in soil and plants could be determined using non-destructive gamma spectrometry techniques as given by many other authors [1, 25].

Results and Discussion

Uranium and Thorium in soil samples

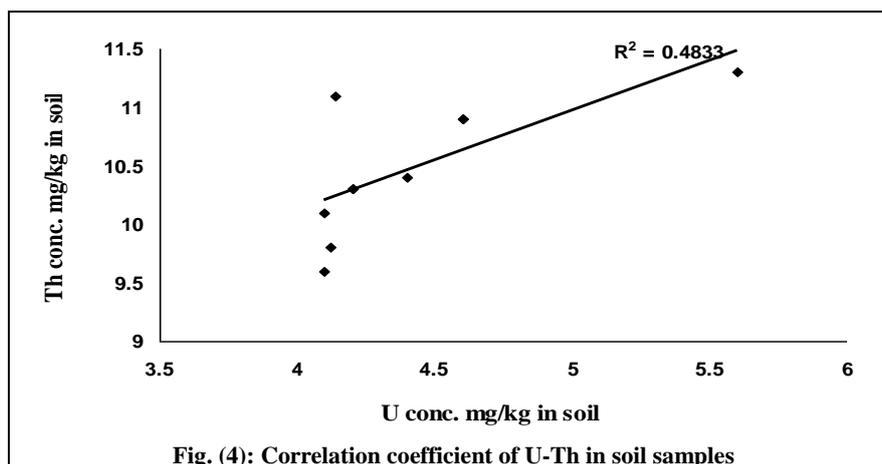
The average concentrations of uranium (U) and Thorium (Th) in Wadi El-Missikat soil are 4.28 - 4.53 mg kg^{-1} for U and 10.26 - 10.7 mg kg^{-1} for Th (Table 1). These values were in agreement with previous values given by Kabata-Pendias and Pendias [26]. The authors mentioned that the worldwide mean of the U content in soils ranges from 0.79 to 11 mg kg^{-1} and the mean of Th, from 3.4 to 13.4 mg kg^{-1} . In this work, the concentration of U in all soil samples varies from 4.1 to 5.6 mg kg^{-1} (Table 1). According to El Hassanin et al. [27], uranium concentrations in similar radioactive soil (G. Qattar area) in North Eastern Desert of Egypt were about 5.1 - 6.9 mg kg^{-1} . These figures coincide with the obtained results of the studied area.

Thorium (Th) concentration shows a narrow range in all soil samples. The highest amount of Th is 11.3 mg kg^{-1} (Table 1), and the lowest value is 9.6 mg kg^{-1} . Correlation coefficient of U-Th in soil samples shows fairly positive correlation ($R^2 = 0.48$). The mineral associations of Wadi El-Missikat stream sediments are represented by radioactive minerals such as thorite and uranothorite besides uranophane (uranium (VI) aluminium silicate) and the radioelements-bearing minerals such as zircon, allanite and fluorite [28]. This may reflect the accommodation of these radioelements in the same minerals such as zircon, uranothorite and allanite with constant ratio during soil formation (Fig. 4).

Table (1): Concentration of Uranium and Thorium (mg kg⁻¹) in dry weight of plant and soil samples and the plant- soil ratio

samples no.	uranium concentration (mg kg ⁻¹)			thorium concentration (mg kg ⁻¹)		
	<i>fagonia sp</i>	soil	ratio	<i>fagonia sp</i>	soil	ratio
1	0.83	4.2	0.2	2.34	10.3	0.23
2	0.95	4.12	0.23	5.7	9.8	0.58
3	1.5	5.6	0.26	2.4	11.3	0.21
4	1.3	4.6	0.28	2.9	10.3	0.26
5	0.74	4.14	0.18	2.3	11.1	0.20
Average	1.06	4.53	0.23	3.13	10.7	0.29

samples no.	<i>zilla sp.</i>			<i>zilla sp.</i>		
	<i>zilla sp.</i>	soil	ratio	<i>zilla sp.</i>	soil	ratio
1	0.25	4.2	0.06	0.64	10.3	0.06
2	0.21	4.1	0.05	0.48	9.6	0.05
3	0.43	4.4	0.11	0.68	10.4	0.06
4	0.48	4.6	0.10	3.61	10.9	0.06
5	0.22	4.1	0.05	0.59	10.1	0.35
average	0.32	4.28	0.07	1.2	10.26	0.12



The averages of activity concentration of U and Th in Wadi El-Missikat soil are 52.86 and 55.97 Bq kg⁻¹ for U and 41.62 and 43.37 Bq kg⁻¹ for Th (Table 2). These values are nearly close to the average abundance of these isotopes in two surface soils in close to the U mills in Italy, U²³⁸ and Th²³² values reach up to 53.7 and 40.1 Bq kg⁻¹, respectively [26].

Uranium and thorium in plants

Uranium in fagonia bovena plant

The average U concentration in plant samples was 1.06 mg kg⁻¹. The highest uptake was 1.5 mg kg⁻¹, while the lowest was 0.74 mg kg⁻¹ (Table 1). Ebyan [14] reported that the average uptake of U

in *fagonia sp.* in Qattar area was 0.84 mg kg⁻¹, indicating the higher absorption ability of the studied species than the world average of plant (WAP). The highest TF was 0.28 in this species, which is more than that was found by Ebyan [14]. The TF of U in *fagonia sp.* reached the value of the WAP that is 46 times as much as that recorded by Sheppard and Eveden [29]. It can be concluded from U analyses in *fagonia* species and underlying soil that the uptake and concentration of U increases in the plant with increasing U concentration in the soil. This conclusion may be confirmed by the positive correlation between U in the plants and in the soil (Fig 5). Reimann et al. [30] mentioned that WAP uptake for U element is

0.01 mg kg⁻¹, suggesting that *fagonia* sp. can absorb and accumulate uranium element 150 times more than the average of world uranium uptake in plants. Chaney et al. [31] indicated that the hyperaccumulator plants can accumulate 10 to 500 times more of an element than ordinary plants. Hence, they are by definition very suitable for phytoremediation. Thus, *fagonia boveana* plant can be used for the exploration and phytoremediation of uranium.

Thorium in *fagonia boveana* plant

Thorium concentrations in *fagonia* sp. are variable. The highest recorded value was 5.7 mg kg⁻¹, while the lowest value was 2.3 mg kg⁻¹ (Table 1). In Qattar area, Ebyan [14] found that the highest concentration was 3.27 mg kg⁻¹ for the same plants, suggesting a higher absorption ability. The

highest recorded TF was 0.58, also suggesting a high accumulation ability in this species. The average of world uptake for Th element is 0.02 mg kg⁻¹ [30]. The studied species can accumulate Th with 285 times more than the average world uptake. Therefore, *fagonia* sp. could be considered a hyper-accumulator plant for Th, according to Chaney et al. [31].

The results obtained indicate that *fagonia* can uptake and accumulate Th more than U (Fig. 6). It is known that U is more mobile in the soil than Th and thus, more bioavailable compared to Th [6], although U and Th exist geologically in same minerals [32]. It is clear that their behavior in living systems may be different. Uranium can form complex compounds [5], which may be rather easily taken up by plants.

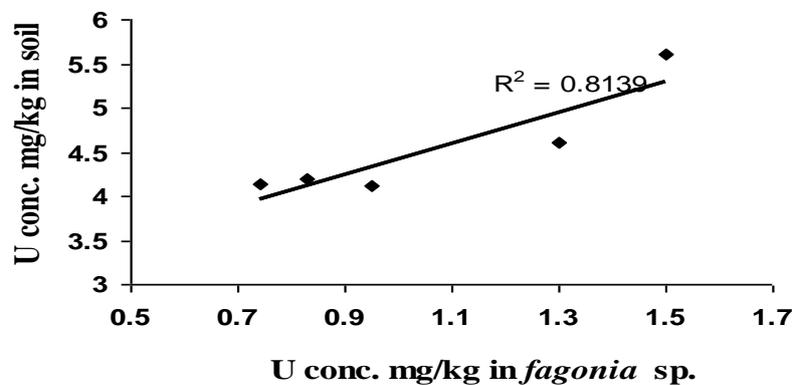


Fig. (5): Correlation of uranium concentration in *fagonia* sp. and underlying soil

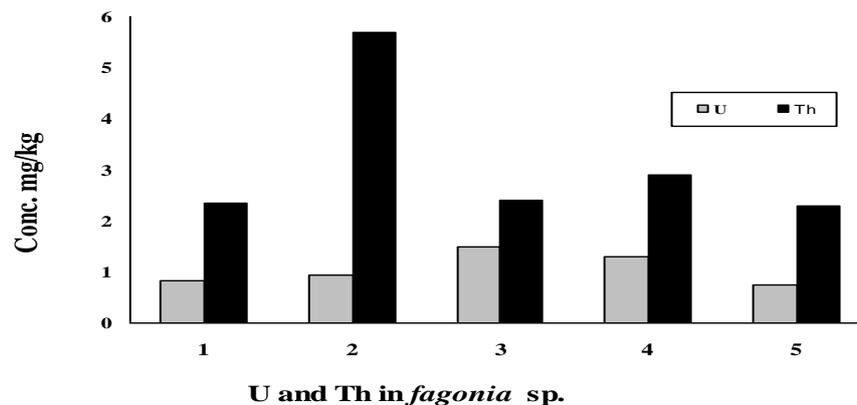


Fig. (6): Histogram showing U and Th accumulation in 5 *fagonia boveana* plant samples

Activity concentration of uranium and thorium in *fagonia* plant

From Table (2), uranium-238 activity concentration in dried *fagonia* sp. samples ranged from 9.14 to 18.53 Bq kg⁻¹ (average value 13.15 Bq kg⁻¹), and thorium-232 activity concentration from 9.34 Bq kg⁻¹ to 23.14 Bq kg⁻¹ (average value 12.7 Bq kg⁻¹). The average activity concentration of uranium and thorium in *fagonia* sp. was 53 and 33 times higher, respectively than that recorded by Termizi et al. [33] for dried grass samples. For leafy vegetables, reference values for U-238 and Th-232 were 0.02 and 0.015 Bq kg⁻¹, respectively, according to the UNSCEAR report [34]. Compared to the activity concentration of uranium in *fagonia* (13.15 Bq kg⁻¹), these values show that *fagonia* contained about 657 times as high activity as the reference values. The estimated average thorium activity concentration of *fagonia* (12.7 Bq kg⁻¹) is about 846 times higher than the reference value.

Finally, from the previous data, the *fagonia boveana* plant is a hyper-accumulator for uranium and thorium

and could be considered a candidate for exploration and phytoremediation of radionuclide-contaminated soils.

Uranium in *Zilla spinosa* plant

U concentrations were determined in plant samples. The highest recorded value was 0.48 mg kg⁻¹, and the lowest value was 0.21 mg kg⁻¹ (Table 1). Ebyan [14] found that the highest concentration of U in *zilla* sp. was 0.55 mg kg⁻¹, which is higher than the contents recorded in the present study. The highest TF is 0.11 which is more than the (0.09) recorded by Ebyan [14]. The calculated TF values reach 22 times more than the average reported in a previous study [29]. Figure (7) demonstrates the positive correlation between U in *zilla* and their underlying soil. *Zilla* sp. can absorb and accumulate U 48 times more than the average value of world plants [30]. Therefore, *zilla spinosa* can also be used in exploration for and phytoremediation of U in other locations.

Table (2): Activity concentration of Uranium and Thorium (Bq kg⁻¹) in dry weight of plant and soil samples and the plant- soil ratio

samples no.	uranium activity (Bq kg ⁻¹)			thorium activity (Bq kg ⁻¹)		
	<i>fagonia sp</i>	soil	ratio	<i>fagonia sp</i>	soil	ratio
1	10.25	51.87	0.20	9.5	41.82	0.23
2	11.73	50.88	0.23	23.14	39.79	0.58
3	18.53	69.16	0.26	9.74	45.88	0.21
4	16.1	56.81	0.28	11.77	44.25	0.26
5	9.14	51.13	0.18	9.34	45.1	0.20
average	13.15	55.97	0.23	12.7	43.37	0.29

samples no.	<i>zilla sp.</i>			soil		
	<i>zilla sp.</i>	soil	ratio	<i>zilla sp.</i>	soil	ratio
1	3.1	51.87	0.06	2.6	41.82	0.06
2	2.59	50.63	0.05	1.95	38.8	0.05
3	5.31	54.34	0.11	2.76	42.22	0.06
4	5.92	56.81	0.10	14.65	44.25	0.33
5	2.72	50.63	0.05	2.4	41.0	0.06
average	3.93	52.86	0.07	4.87	41.62	0.12

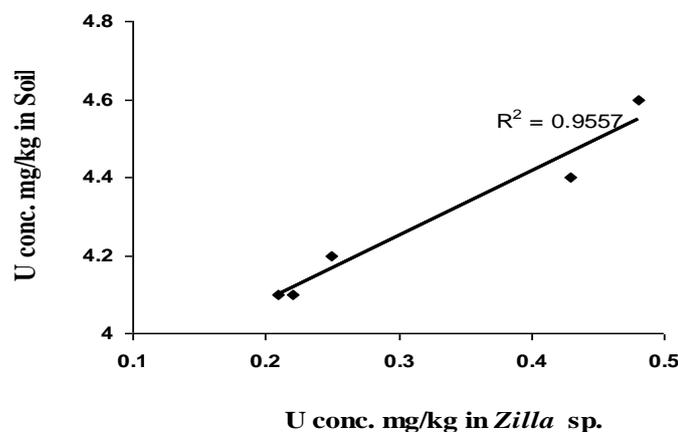


Fig. (7): Correlation of uranium concentration in zilla sp. and underlying soil

Thorium in zilla spinosa plant

The highest recorded value for Th was 3.61 mg kg⁻¹ (Table 1), which is more than that recorded by Ebyan [14], who reported that the highest value of Th in *zilla spinosa* was 0.55 mg kg⁻¹. The highest TF was found to be 35, which is also more than that reported by Ebyan [14]. On the other hand, *zilla sp.* absorbs and accumulates Th with 181 times more than the average world uptake. There is a fair correlation between Th in *zilla* and underlying soil (Fig. 8). The relative decrease of the correlation coefficient for the absorption of thorium in *Zilla Spinosa* (R= 0.628) is due to the

increased absorption of the element in one of the samples (sample 4), unlike the rest of the samples. This increase in absorption is due to the presence of the plant species in a low-lying part of the studied area, which led to the slow flow of rain water that provided a greater capacity to absorb. Also, *zilla sp.* can uptake and accumulate Th more than U (Fig. 9). From the previous data, it was found that both studied species *fagonia* and *zilla* can absorb and accumulate uranium and thorium but *fagonia* shows the better TF.

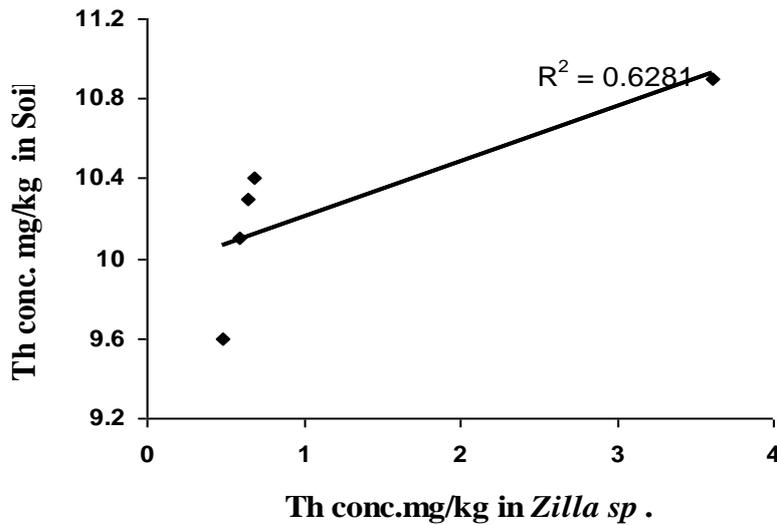


Fig. (8): Correlation of thorium concentration in *zilla sp.* and underlying soil

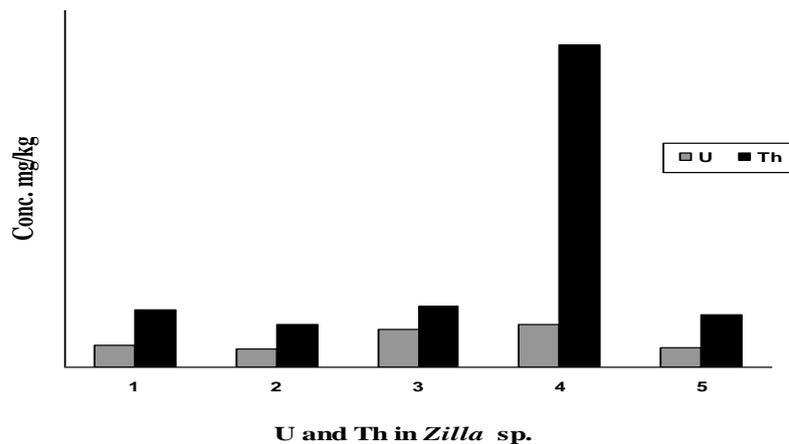


Fig. (9): Histogram showing U and Th accumulation in 5 *zilla spinosa* plant samples

Activity concentration of uranium and thorium in zilla plant

The activity concentration of uranium 238 in *zilla* sp. ranged from 2.59 to 5.92 Bq kg⁻¹ (mean 3.93 Bq kg⁻¹) and thorium activity from 1.95 to 14.65 Bq kg⁻¹ (average 4.87), (Table 2). The average of activity concentration of uranium and thorium in *Zilla* sp. reached 196 and 325 times, respectively, more than values of the world plant average recorded by the UNSCEAR report [34]. From the previous data, it was found that both species (*fagonia* and *zilla*) can absorb and accumulate uranium and thorium, but *fagonia* has a greater ability.

Cultivation of the species under study could be carried out by seedling and seed. According to [35], some natural or wild plants such as *Trichodesma africanum*, *Cotula cinerea*, *Zilla spinosa* and *Zygophyllum coccineum* may be planted by seedling and seed, but the seedling growth is preferable. Therefore, the planting of these species in polluted soil can help in its remediation.

Conclusion

The specific activities and concentrations of U and Th were determined for Wadi El Missikat area soil and plants. Notable biogeochemical relations between the uranium and thorium contents in soil and in plants growing on them indicate a positive correlation. A comparison of uranium and thorium uptake and accumulation by *fagonia* and *zilla* plants with world plant averages (WPA) revealed that the species under investigation are hyper-accumulators and may be used for exploration and phytoremediation of radioactive elements such as uranium and thorium. Finally, grazing in the studied area does not represent any hazard where these plants are sporadic and grow only in a part of the year, but their ability to uptake these elements increases their importance in the remediation of polluted areas.

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