Determination of Total and Bioavailable Fractions of Radionuclides and Trace Metals in Soil and Plants by ICP-AES

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Abstract - **The study was carried out on the physicochemical analysis and bioavailability studies of natural radionuclides like uranium-238 and thorium-232 and trace metals such as barium, copper, iron, manganese, molybdenum and zinc collected in and around uranium corporation of India limited, Thummalapalli, Cuddapah district of Andhrapradesh. The physical and chemical parameters like pH, EC, TDS, phosphorous and potassium were studied, tabulated and briefly discussed. The Soils of the cuddapah district are of two types, i.e., red ferruginous and black soils. Black clay is the most superior soil in the District, Which occupies 23.7% area in the District. The physical properties and high amount of phosphorous and potassium indicates the soil contamination from mining and domestic activities which may results to the entering of these radionuclides and trace metals in the human food either water or plants. The results obtained clearly indicated that the natural radionuclide uranium-238 was accumulated in all the collected plant species and found more in the leaves, whereas a negligible concentration of thorium was found in all the plants.**

Keywords - bioavailability, natural radionuclides, trace metals, mining.

I. INTRODUCTION

Radionuclide composition is one of the important characteristics of the environment and its determination is necessary for solving wide range scientific and practical problems. Natural radionuclides can enter the environment as a result of natural washing out and weathering processes of rocks and due to the rapid growth of mining industry in the last century. Uranium and thorium are major energy sources, which drive the evolution of Earth and planets. Both these radionuclides are components of the biosphere, and thus occur naturally in all soils and plants, though their concentrations in plants may be rather low. There are numerous reports in literature on biogeochemistry of U and Th [1-9]. Unfortunately, large part of available publications refers to the studies performed either in highly contaminated areas or in nutrient solutions that have been artificially 'spiked' with radionuclides. Meanwhile, it would be more important to assess the effects of background levels of natural radioactivity on soil and plants.

The study of uranium and thorium transfer from soil to edible vegetation through root uptake is very important, especially considering accumulation of these radionuclides in the food chains. An understanding of the mobility of uranium and thorium in soils and their transfer to different plants requires a detailed knowledge of uranium and thorium interactions with soil composed of abiotic and biotic components. Despite numerous studies on uranium and thorium contents in vegetation, there is little information yet related to the rate of their uptake and storage by different plant species. Previous experimental results demonstrated that distribution of uranium and thorium in soil is highly variable. For example, activity concentrations of 238-U in soil can vary by around three orders of magnitude depending on various factors [10]. Therefore, an assessment of the radionuclide distributions in the soil–plant system may be rather complicated.

The concentration of radionuclides and trace metals in the environment can be measured by means of various chemical as well as instrumental methods. Studies of radionuclides in the environment have entered a new era, in the face of renaissance of nuclear energy and concerns about national security with respect to nuclear nonproliferation [11]. In the present scenario the analysis of natural radionucluides and trace metals received a great concern as it is difficult to manage the contaminants in the environment and has become a complex and challenging problem with worldwide ramifications. The knowledge of fixation of radionuclides and trace metals by the soils is of great importance, because the adsorption processes determine to a considerable extent the transport and availability of the trace and radio pollutants.

The present study focused on the bioavailability of natural radionuclides and heavy metals in chosen soil – plant systems. The most common methods used nowadays for the determination of heavy metals in environmental samples involve highly sensitive spectroscopic techniques, such as atomic absorption spectrophotometer (AAS), neutron activation analysis (NAA) and inductively coupled plasma optical emission spectrophotometer (ICP-AES). Soil acts as an important reservoir for heavy metals, which leads to the following question: to what extent are these soils bound metals available for uptake by living organisms (bioavailable)? Concentrations of heavy metals in soil usually exceed those of the overlying water by between three and five orders of magnitude [12]. With such high concentrations, the bioavailability of even a small fraction of the total metal in soil assumes considerable importance.

The heavy metal pollution has become one of the most serious environmental problems today. The effects of heavy metals depend on the mobility of each metal through environmental compartments and the pathways by which metals reach humans and the environment. The degree of concern about human and environmental health varies with each metal and some metals are toxic and others are known to be essential micronutrients for humans and animals.

Metal bioavailability results in high concentrations of the corresponding metals in biota, through the so-called bioconcentration process. While considering the trace elements in plants, the extra dimension compared with the elements in air, water and soil, is the wide range of species. Therefore, it is not straightforward to generalize over concentrations and effects. Trace elements have been considered essential to plant survival [13-15]. The incorporation of metals into plants is mainly achieved by uptake from the soil through the roots. The uptake may also occur from deposits of the heavy metals on the leaves from soil or aerosol [16-19]. Previous studies are confined to limited number of elements [20, 21].

Bioconcentration is referred to as the process by which a chemical species is accumulated into biota from its surrounding phases. The bioconcentration factor (BCF) and transport index (Ti) that is used to calculate the distribution of heavy metals between soil and biota is defined as follows

$$BCF = \frac{C_{Biota}}{C_{Soil}}$$

Where, C_{Biota} is the total metal concentration in biota (µg/g) and

C_{Soil} is the total metal concentration in soil (µg/g).

$$Ti = \frac{C_{Leaf}}{C_{Root}}$$

Where, C_{Leaf} is the concentration of metal in leaf (µg/g) and

C_{Root} is the concentration of metal in root (µg/g)

The aim of the study is to determine the radionuclide and metal concentrations in chosen soil – plant system, including relationships between these radionuclides in soil and in plants and temporal changes of uranium and thorium concentrations in different plant species.

II. MATERIALS AND METHODS

2.1. Study Area

Cuddapah district occupies an area of 15,938 square kilometers (6,154 sq mi). The District was first formed in early 19th century during the British rule. It is surrounded by Kurnool District on the North, Chittoor District on the South, Nellore on the East and Anantapur on the West between the 13 $43^0$and 15 10^0Northern Latitudes, 77 $55^0$and 79 29^0 of the Eastern Longitude. The Majority of the people here depend on Agriculture for livelihood. The Major crops in the District are paddy, Groundnut, Sunflower, Cotton, Betel leaves and Horticultural crops like Mango, Papaya, Banana, Lemon and Oranges. The gross cropped area in the district is 472511 Hectares out of this gross irrigated area is 192832 Hectares. The Soils in the District are of two types, i.e., Red Ferruginous and Black Soils. Black Clay is the most superior soil in the District, Which occupies 23.7% area in the District.

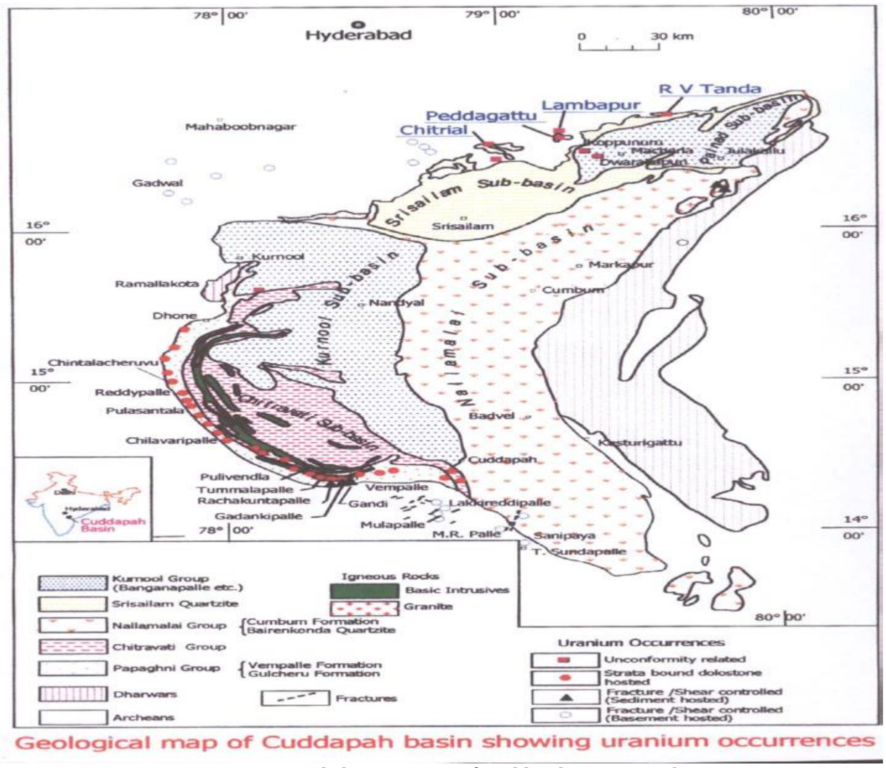


Figure 1 General characteristics of Cuddapah District, India.

2.2. Location & Geographical Area

The Geographical area of the District is 15,359 Sq.Kms. with 3 Revenue Division, 51 Mandals, 804 Gram Panchayats, 1032 Revenue villages and 4954 Habitations. The Cuddapah is surrounded by Kurnool District on the North, Chittoor District on the South, Nellore on the East and Anantapur on the West and graphically represented in Figure 1.

2.3. Topography

Cuddapah District is also considered to be one of the district endowed with rich history are minerals Flora & Fauna. Hyder Ali, Tippu Sulthan, Sivaji, Krishnadevaraya and Pratapa Rudra are some of the names associated with the History of tract. The district is blessed with a series of beautiful valleys through which Papagni, Chitravathi, Mandavya, Penna and cheyyuru rivers flow.

III. SAMPLING AND ANALYSIS

3.1. Sampling Stations - The following three sampling stations were selected for the present study located in and around Thummalapalli, Cuddapah District of Andhrapradesh.

1. Uranium Corporation of India Limited, Thummalapalli
2. Besthavaripalli
3. Mabbuchintalapalli

IV. SAMPLE COLLECTION AND ANALYSIS

4.1. Soil Samples

Surface soil samples (30 cm depth) were collected in metal free polyethylene bags from the area adjacent to the plant roots. The pH was determined in aqueous extract 1:2. Organic matter was determined by a colorimetric method using $K_2Cr_2O_7$, H_2SO_4 and saccharose solution as standard solution. Total P was determined by elemental analysis. Electrical conductivity was measured by digital conductivity meter (Elico CM 180), with a cell constant value of 1.0. For the determination of trace metals, soil samples were dried at 40^0 C to constant weight, sieved to a particle size of 2 mm, subjected to microwave acid digestion (Milestone ETHOS ONE) with HNO_3: HCL: H_2O_2:HF (4:1:3:2) and evaporate to dryness to remove Hydrogen fluoride.

4.2. Plant Samples

Four native plant species named *Pedalium murex* L., *Datura metel* L., *Arachis hypogaea* L. and *Solanum melongena* L. were collected in metal free polyethylene bags in and around Uranium corporation of India limited, Besthavaripalli and Mabbuchintalapalli villages of Cuddapah District. The collected plants were washed with running tap water in order to remove the adhering soil particles and then separated into leaves, stems and roots, dried at 60±50^0 C until constant weight and then ground and sieved. Later samples were kept for ashing in a muffle furnace (PYRO, Milestone) to remove the carbon content then digested with HNO_3: HCL: H_2O_2 (10:2:5).

V. RESULTS AND DISCUSSION

The prepared soil and plant samples (Leaves, Stem and Roots) their physical, chemical parameters, radionuclide and trace metal concentrations have been analyzed by Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Horiba Jobin YVON) and the results were tabulated in Tables 1-5.

5.1. pH

pH is the hydrogen ion concentration and is an indicator of the acidity or basicity of the sample. It is the most important test used to study the soil chemistry. It has been observed that the pH concentrations of Thummalapalli soil sample collected near Uranium mining ore showed higher (pH=8±0.3) which may be attributed due to petrifaction and decomposition of organic matter.

High carbonates and bi-carbonates cause Calcium and Magnesium ions to form insoluble minerals leaving Sodium as the dominant ion in solution. Highly alkaline water can intensify soil conditions, which will have implications for agriculture. The pH analysis of soil samples shows a maximum of 8.0 at Thummalapalli and minimum of 7.6 at Besthavaripalli as shown in Figure 2. Slightly alkaline pH could be attributed to all the samples and in cases of alkalinity due to the industrial effluent, and may be food stuff from domestic sources.

Table 1 Physico-chemical characteristics of soil.

S.No.	Parameters	Thummalapalli	Besthavaripalli	Mabbuchinthalapalli
1	pH	8.0 ± 0.3	7.6 ± 0.2	7.7 ± 0.3
2	Electrical Conductivity	1.46 ± 0.16	1.37 ± 0.34	1.50 ± 0.02
3	TDS	0.87 ± 0.06	0.82 ± 0.11	0.9 ± 0.04
4	Organic carbon	17.0 ± 9.91	17.5 ± 7.22	17.1 ± 9.84
5	P (%)	2.0 ± 0.12	3.0 ± 0.04	2.0 ± 0.11
6	K (%)	0.04 ± 0.01	0.06 ± 0.02	0.14 ± 0.05

Values are means ± standard deviations, n=3

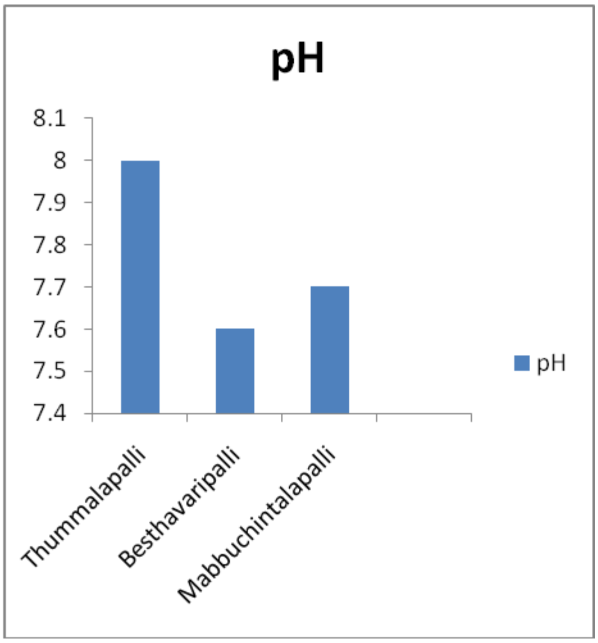


Figure 2 pH of soil samples.

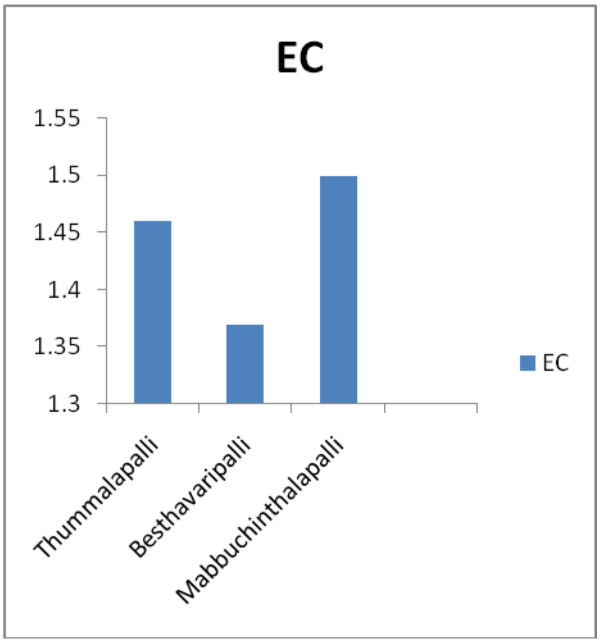


Figure 3 Electrical conductivity of soil samples.

5.2. Electrical Conductivity

Electrical conductivity (EC) is a measure of the ions present in sample, the conductivity increases with the increase of ions. It is also effectively a surrogate for Total dissolved Solids (TDS) and is important for irrigation because it is a measure of the salinity of the sample. The Electrical conductivity of soil sample used for irrigation showed 1.50 dS/m at Mabbuchintalapalli and minimum of 1.37 dS/m at Besthavaripalli. The EC values of three samples lie within the FAO irrigation water quality standards and shown in Figure 3.

5.3. Total Dissolved Solids

TDS refer to the matter suspended or dissolved in water or wastewater. Solids may affect waste and or effluent quality adversely. A constant level of minerals in the soil is necessary for plant life. Concentrations of total dissolved solids that are too high or too low may have limited the growth and lead to the death of many plants. The TDS of soil samples shows range between 0.82 mg/L at Besthavaripalli to 0.90 mg/L. at Mabbuchintalapalli. The soil sample of Mabbuchintalapalli has more TDS, which is understandable because suspended materials along with the salts are not settled completely. Excessive total salt concentration or excessive levels of some potentially toxic elements can have detrimental effects on plant health and soil conditions. The concentration of TDS of soil samples was graphically represented in Figure 4.

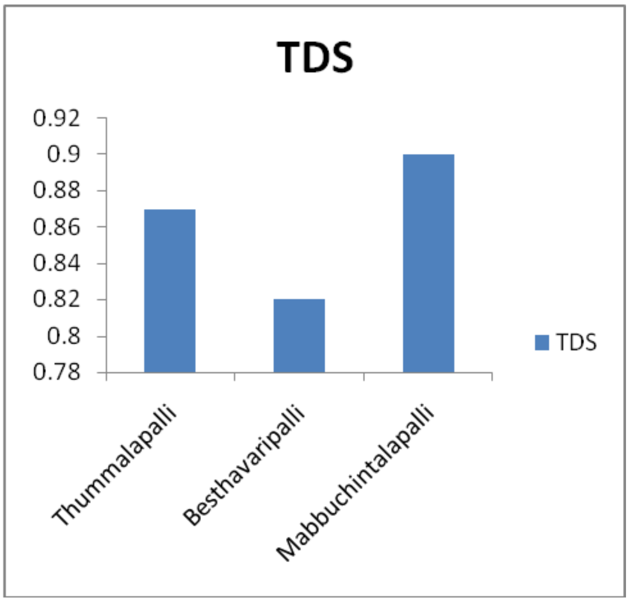


Figure 4 Total dissolved solids in soil samples

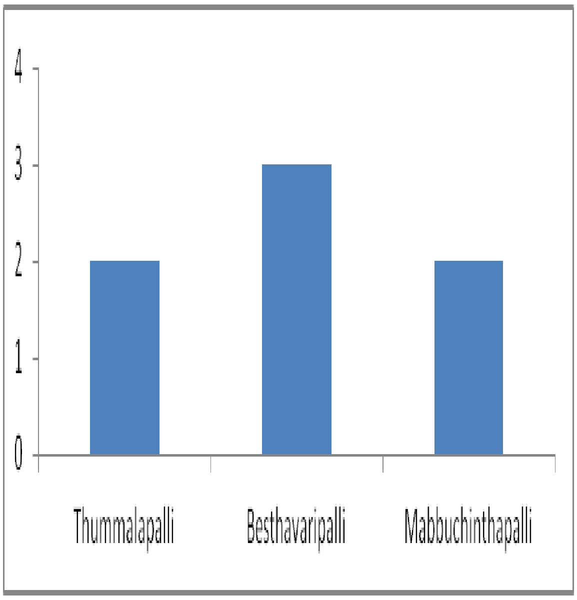


Figure 5 Available Phosphorous in soil samples.

5.4. Available Phosphorous

Phosphorus is also a primary macronutrient that is essential to the growth of plants and other biological organisms but quantities can be excessive and if the concentrations in water are too high noxious algal blooms can occur. Phosphates are classified as orthophosphates, poly-phosphates and organic phosphates. The Phosphorous of three soil samples varied from 2.00% in Thummalapalli and Mabbuchintalapalli to 3.00% at Besthavaripalli and represented in Figure 5. However values of Phosphorous at three locations are slightly exceeds but it is safe range of restriction on use of FAO irrigation water quality standards.

5.5. Potassium available

Potassium is not an integral part of any major plant component but it does play a key role in a vast array of physiological processes vital to plant growth, from protein synthesis to maintenance of plant water balance. Potassium is a macro nutrient that is present in high concentrations in soils but is not bio-available since it is bound to other compounds. Potassium may originate from human faeces and urine disposal, as human faeces has on average 1.6% and urine has 3.7% (dry weight) potassium. The present study showed that the concentration of Potassium in soil samples has maximum of 0.14% at Mabbuchintalapalli and minimum of 0.04% in Thummalapall and graphically represented in Figure 6. However concentration Potassium at three locations is exceeds of restriction on use of FAO irrigation water quality standards. The main reason may be solid wastes from the uranium corporation of India limited, Thummalapalli are dumping near the premises and their degradation.

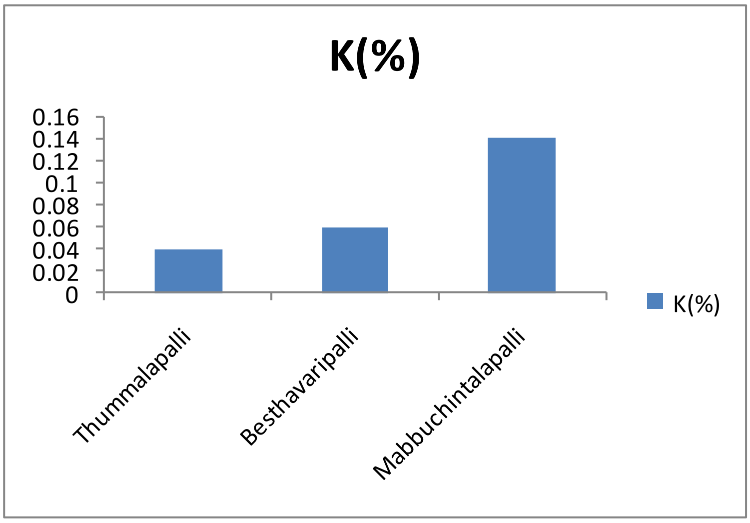


Figure 6 Potassium available in soil samples.

5.6. Bioavailability of natural radionuclides and trace metals in medicinal plants Pedalium Murex L. *and Datura metel* L. *and their respective soils*

The natural radionuclide's (U-238 and Th-232) and trace metals (barium, copper, iron, manganese, molybdenum and zinc) were detected in the soil samples collected at Thummalapalli and also various growing sites of *Pedalium murex* L. and *Datura metel* L. All the obtained elemental soil profile of both the plants was tabulated in the Tables 2 and 3. Trace metal concentrations in both the plants was represented in Figures 7 and 8. It clearly shows that both the plants accumulate high amounts of zinc that too concentrated in the leaves than the remaining parts. In soil samples, only zinc showed the highest metal concentration among other trace elements followed by barium and iron. Uranium was found to be high in soil sample 2 which is collected at uranium corporation of India limited, Thummalapalli. Natural radionuclide and trace metal concentrations of all the soil and plant samples was represented in Figures 11, 12 and 13. In *Pedalium murex* L. uranium was found to be 6 µg/g and 3 µg/g in the leaves and roots, whereas in *Datura metel L.* uranium was found to be 12 µg/g and 4 µg/g in leaves and roots respectively.

Figure 11 reveals that high concentrations of uranium was found in the leaves and roots of *Datura metel L.* and negligible amount of uranium is found in the stem of *Pedalium murex* L. and *Datura metel L.*. Bioconcentartion factor and transport index of soil and plant samples was investigated, the results showed that the plant species can be used as a hyper acculumulators as the transport index is more than one for all determined trace elements. Overall, the highest radioactivity concentrations in plants are found in those collected in area with the highest radioactive concentration in the soil substrate and the lowest in those with lowest concentration in the substrate.

Table 2 Bioavailability of natural radionuclides and trace metals in medicinal plant *Pedalium murex* L. and their respective soil.

Sample	Ba	Cu	Fe	Mn	Mo	Zn	U-238	Th-232
Soil	276±12	23±3	931±21	72±7	ND<21	3.43%	91±7	22±1
Leaves	58±6	9±2	249±9	54±10	ND<4	2405±19	6±1	ND<0.2
Stem	34±3	ND<5	21±3	15±2	ND<4	250±5	ND<4	ND<0.2
Root	14±5	2±0.3	34±7	12±2	ND<4	436±9	2±0.5	ND<0.2
BCF	0.21	0.39	0.26	0.75	-	0.70	0.06	-
Ti	4.14	4.5	7.32	4.5	-	5.5	3.0	-

Values are means ± standard deviations, n=3

Table 3 Bioavailability of natural radionuclides and trace metals in medicinal plant *Datura metel* L. and their respective soil.

Sample	Ba	Cu	Fe	Mn	Mo	Zn	U-238	Th-232
Soil	324±11	32±2	1103±37	88±6	ND<21	3.18%	97±4	18±2
Leaves	43±3	11±0.3	369±12	27±2	ND<4	2216±21	12±2	ND<0.2
Stem	28±5	6±1	78±7	15±3	ND<4	316±9	ND<4	ND<0.2
Root	18±4	4±0.6	23±3	11±2	ND<4	184±6	4±0.1	ND<0.2
BCF	0.13	0.34	0.33	0.30	-	0.69	0.12	-
Ti	2.38	2.75	6.04	2.45	-	5.04	3.0	-

Values are means ± standard deviations, n=3

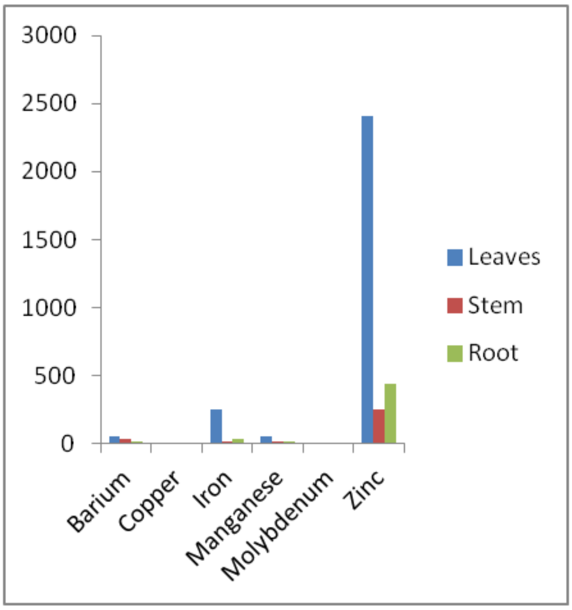


Figure 7 Trace metal concentrations (µg/g) in *Pedalium murex* L.

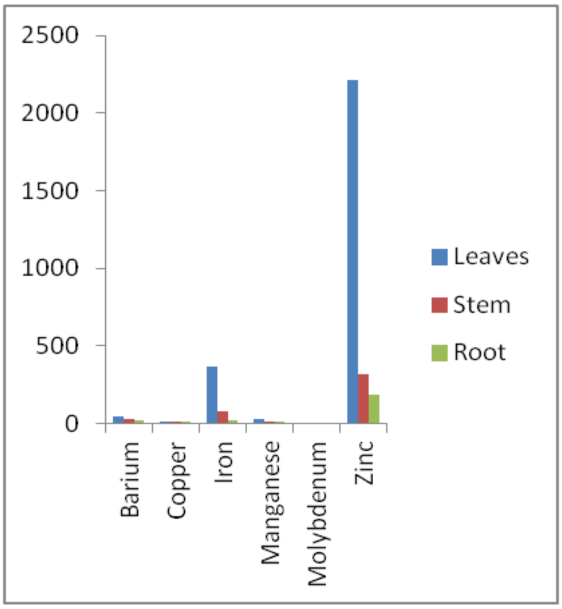


Figure 8 Trace metal concentrations (µg/g) in *Datura metel* L.

5.7. Bioavailability of natural radionuclides and trace metals in Edible plants Arachis hypogaea L. *and Solanum melongena* L. *and their respective soils*

The natural radionuclides and trace metals were determined in both the edible plants and their corresponding soils. All the obtained elemental soil profile of the plant species was tabulated in the Tables 4 and 5. Figure 13 clearly shows that only zinc showed the high metal concentration among all the soil samples and in the plant samples barium was found to be high in the leaves and molybdenum was detected only in the root of *Arachis hypogaea* L according to Figures 9 and 10 respectively. As shown in Figure 11, similar concentrations of uranium was found (4 µg/g) in the leaves and negligible concentrations was found in the stem of *Arachis hypogaea L.* and *Solanum melongena* L. Bioconcentration factor and transport index of soil and plant samples was investigated, the results showed that the plant species can be used as a hyper accumulator for copper and Uranium as the transport index found to be greater than one. This study reveals that different plant species uptake different amount of radionuclides depending on the substrate concentration, nature, ageing as well as their soil type and climatic conditions. The obtained values show that the concentrations of radionuclides in plant organs differ significantly.

Table 4 Bioavailability of natural radionuclides and trace metals in edible plant Arachis hypogaea L. and their respective soil.

Sample	Ba	Cu	Fe	Mn	Mo	Zn	U-238	Th-232
Soil	880±22	15±1.5	870±16	81±9	ND<21	3.18%	81±5	17±1
Leaves	25±3	3±0.3	ND<2	24±4	ND<4	325±9	4±1	ND<0.2
Stem	35±6	1±0.2	ND<2	5±2	ND<4	121±8	1±0.3	ND<0.2
Root	28±4	2±0.3	ND<2	28±2	46±6	ND<7	2±0.6	ND<0.2
BCF	0.02	0.2	-	0.02	-	4.01	0.03	-
Ti	0.89	1.5	-	0.85	-	-	1.5	-

Values are means ± standard deviations, n=3

Table 5 Bioavailability of natural radionuclides and trace metals in edible plant Solanum melongena L. and their respective soil.

Sample	Ba	Cu	Fe	Mn	Mo	Zn	U-238	Th-232
Soil	2232±36	9±0.5	499±13	221±13	263±12	1.91%	55±8	10±1
Leaves	370±13	4±1.3	11±3	23±3	ND<4	ND<7	4±1	ND<0.2
Stem	126±6	3±0.7	ND<2	60±4	ND<4	13±3	ND<4	ND<0.2
Root	123±10	3±0.3	7±2	33±5	ND<4	13±4	3±0.6	ND<0.2
BCF	0.16	0.44	5.75	0.04	-	-	0.07	-
Ti	3.01	1.33	1.57	0.69	-	-	1.33	-

Values are means ± standard deviations, n=3

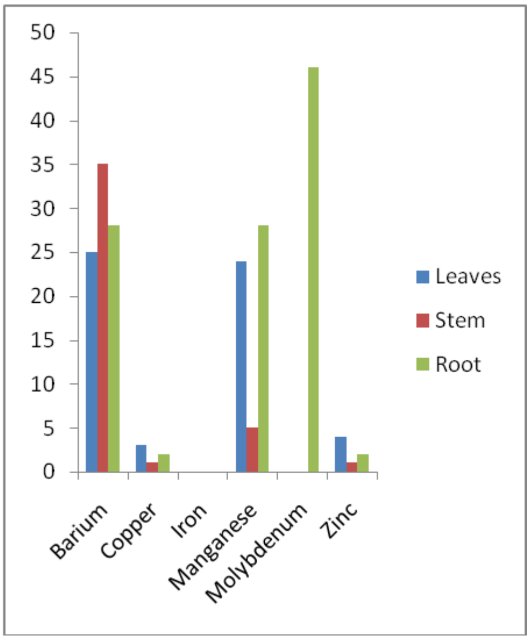


Figure 9 Trace metal concentrations (µg/g) in *Arachis hypogaea* L.

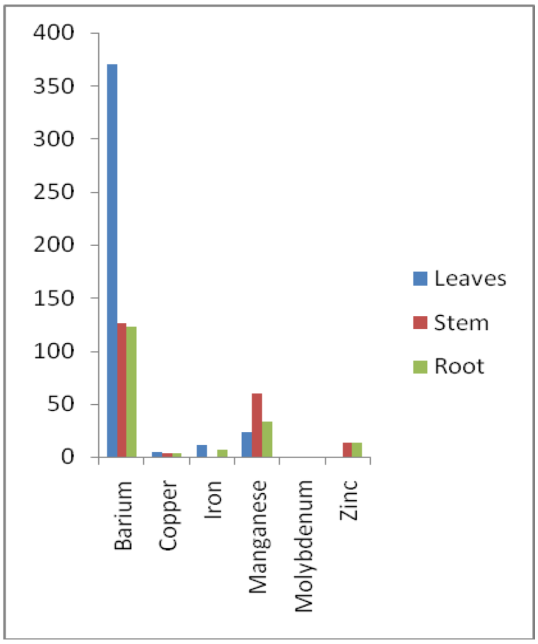


Figure 10 Trace metal concentrations (µg/g) in *Solanum melongena* L.

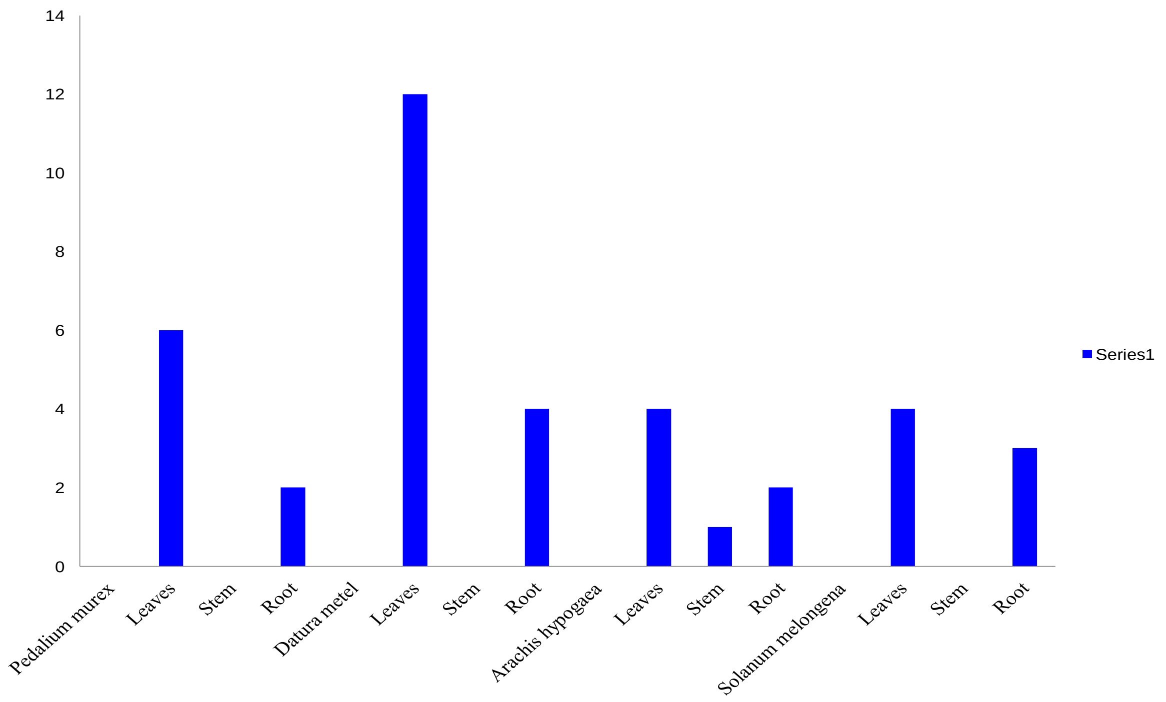
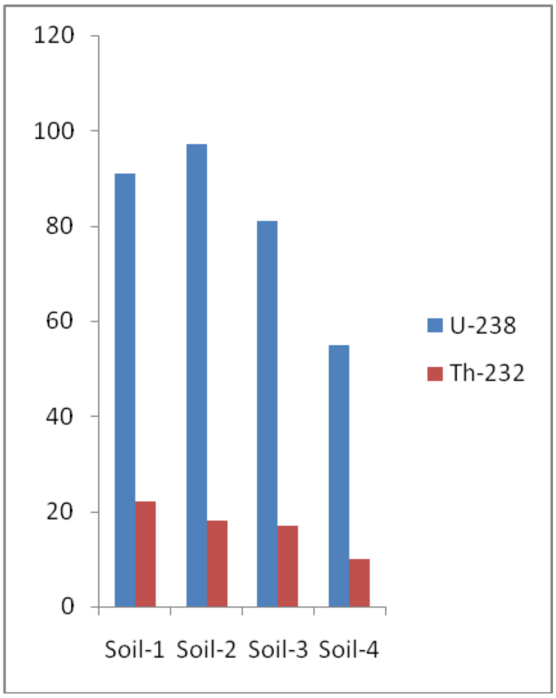


Figure 11 Uranium concentration (µg/g) in plant samples



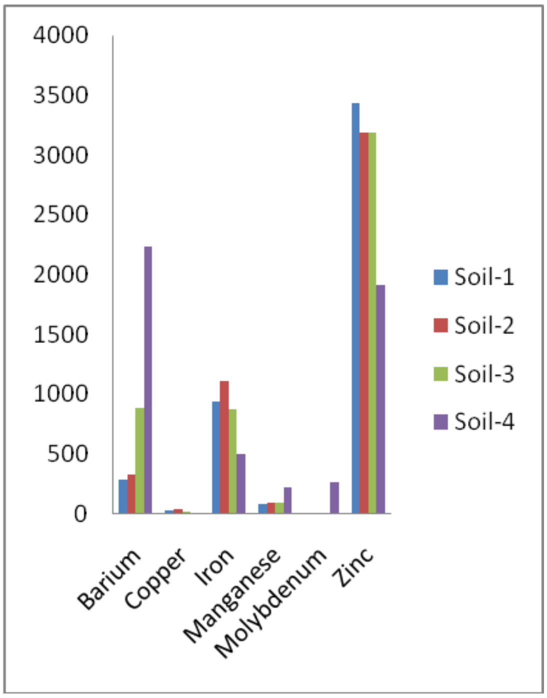


Figure 12 Natural radionuclides concentration (µg/g) in soil samples

Figure 13 Trace metals concentration (µg/g) in soil samples

REFERENCES

[1]. Sheppard, S.C., Evenden, W.G., 1988. The assumption of linearity in soil and plant concentration ratios: an experimental evaluation. J. Environ. Radioact. 7,221–247.

[2]. Mazor, E., 1992. Uranium in plants of Southern Sinai. J. Arid Environ. 22, 363–368. McLung, C.R., 2001. Circadian rhythms in plants. Annu. Rev. Plant Physiol. Plant Mol. Biol. 52, 139–162.

[3]. Mortvedt, J.J., 1994. Plant and soil relationships of uranium and thorium decay series radionuclides – a review. J. Environ. Qual. 23, 643–650.

[4]. Voigt, G., Scott, E.M., Bunzl, K., Dixon, P., Sheppard, S.C., Whicker, W.F., 2000. Radionuclides in the environment: radiological quantities and sampling designs. Radiat. Prot. Dosimetry 92, 55–57.

[5]. Vera Tome´ , F., Rodrigues, P.B., Lozano, J.C., 2002. Distribution and mobilization of U, Th and 226Ra in the plant–soil compartments of a mineralized uranium area in South- west Spain. J. Environ. Radioact. 59, 223–243.

[6]. Vera Tome´ , F., Rodrigues, P.B., Lozano, J.C., 2003. Soil-to-plant transfer factors for natural radionuclides and stable elements in a Mediterranean area. J. Environ.Radioact. 65, 161–175.

[7]. Thiry, Y., Schmidt, P., VanHees, M.,Wannijn, J., VanBree, P., Rufyikiri, G., Vandenhove, H., 2005. Uranium distribution and cycling in Scots pine (Pinus sylvestris L.) growing on a revegetated U-mining heap. J. Environ. Radioact. 81, 201–219.

[8]. Tsuruta, T., 2006. Bioaccumulation of uranium and thorium from the solution containing both elements using various microorganisms. J. Alloys Compd. 408–412, 1312–1315.

[9]. Galindo, C., Mougin, L., Fakhi, S., Nourreddine, A., Lamghari, A., Hannache, H., 2007. Distribution of naturally occurring radionuclides (U, Th) in Timahdit black shale (Morocco). J. Environ. Radioact. 92, 41–54.

[10]. Ewers, L.W., Ham, G.J., Wilkins, B.T., 2003. Review of the Transfer of Naturally Occurring Radionuclides to Terrestrial Plants and Domestic Animals. National Radiological Protection Board Report, NRPB-W49. Chilton, pp. 1–64.

[11]. Journal of Environmental radioactivity, Volume 101, Issue 6, Pages 425-518 (June 2010). International Conference on Biogeochemistry of Trace Elements), Beijing, China, July 2007.

[12]. Bryan and Langston, Environmental pollution, 1992;76(2):89-131. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review.

[13]. Aidid, S.B., J. Radioanal. Nucl. Chem., 120**,** 335 (1988).

[14]. Samudralwar, D.L. and Garg, A.N., Acta Agron. Hung, 42, 77 (1993).

[15]. Kanias, G.D. and Dhilianos, S.M., J. Radioanal. Chem., 52, 389-397 (1979).

[16]. Brown, H.J.M., Environmental Chemistry of the Elements, Academic Press (1979).

[17]. Brooks, R.R., Biological Methods of Prospecting for Minerals, Wiley ; (1983).

[18]. Kabata-Pendias, A. and Pendias, H., Trace elements in soils and plants**.** CRC Press (1984).

[19]. Ray, P.M., The Living Plant, 2nd Ed., Holt Rinehart and Winston (1972).

[20]. Rajurkar, N.S., Shah, N.P. and Purushottam, J., Appl. Radiat. Isot., 41(6), 579 (1990).

[21]. Cunningham, W.C. and Anderson, D.L., Trans. Am. Nucl. Soc., 65, 141 (1992).