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NATURAL ACTINIDES STUDIES IN CONIFERS GROWN ON URANIUM MINING DUMPS (THE EAST CARPATHIANS, ROMANIA)

Lucian PETRESCU[a] & E. BILAL[b]

[a] *University of Bucharest, Faculty of Geology et Geophysics, Department of Mineralogy, 1 N.Balcescu Ave., 010041 Bucharest 1, Romania; fax +40213181557; lucpet@geo.edu.ro*
[b] *Ecole Nationale Supérieure des Mines, Département GENERIC, 158 cours Fauriel, 42023 Saint Etienne, France; fax +33477420163; bilal@emse.fr*

Abstract

A study of U, Th and Sr distribution in soils and conifers was realized at the Crucea area (northern Romania). The increased concentration of U and Th in the surfaced soils is related to dispersion of those elements from wastes. The bioavailability of the metals from the soil (EDTA extraction) decrease in the following order: Th(21,91%) > U(6,20%) > Sr(3,01%).

The fir *Abies alba* and the spruce *Picea excelsa* were found to have a high uptake capacities of uranium. Analyses of the evergreen vegetation indicated that in general uranium is preferentially concentrated in the roots, followed by the twigs and leafs/needles. For the behavior of Th and Sr, we noticed that they in the first place concentrate mainly in the root that is just like in the case of U. Sr shows a different behavior. Sr is in conifers found to be more concentrated in needles and twigs than in roots and stems.

Since the plants do not need U and Th neither for their metabolism, nor for their structure, it follows that the assimilation of these elements is being done through passive processes. The passive absorption implies the diffusion of uranyl ions and organically bound Th^{4+} from the soils in the endodermis of the roots, do to their imperfect selectivity and increased of permeability of cell membranes.

The behaviors of *Abies alba* and *Picea excelsa* are very interesting because they can reach and accumulate U, Th and Sr over very long periods of time. Consequently, planting conifers on uranium waste slopes may decrease the U, Th and Sr migration. The evergreens trees have a high potential of diminishing the quantity of mobile natural radioactive elements through bioaccumulation.

Keywords: U-mining, conifers, U, Th, Sr, phytostabilization

1. INTRODUCTION

Natural actinides (Th and U) are relatively scarce in the earth materials. According to Marshall & Fairbridge (1999) their normalized natural abundances in the earth's crust are relatively low (6 and 1.8 ppm for Th and U, respectively, in crustal rocks) but are higher than those of Ag or Hg. Uranium deposits are known on all continents. Natural radioactive metals leached from wastes materials contaminate surrounding groundwater, soils and biota. U and Th should be immobilized in order to protect the environment. Phytoremediation is a promising technique used for rehabilitation of the radioactive contaminated lands [Entry et al. (1996)]. Unfortunately, the main disadvantage of the phytoremediation techniques is the long time required for clean-up of metal contaminated soils. Phytostabilization is attractive to reduce bioavailability and offsite migration of contaminants [Berti & Cunningham (2000)]. Unlike other phytoremediative techniques, the goal of phytostabilization is not to remove metal contaminants from a site, but rather to stabilize them and reduce the risk to human health and the environment.

Some plants have the capacity to preferentially concentrate uranium at higher level than it might be in the surrounding soil, without prejudicial effects [Shtangeeva et al. (2005), Sheppard et al. (1992)]. Several studies relevant to radionuclide (U and Th) accumulation by plants have been conducted on the relationship between plants and soils [Shtangeeva et al. (2005), Shtangeeva & Ayrault (2004), Petrescu & Bilal (2003), Rufyikiri et al. (2002), Shahanded & Hosner (2002), Huang et al. (1998), Zararsiz et al. (1997), Popescu et al. (1997), Entry et al. (1996), Cornish et al., (1995), Saric et al. (1995), Miekeley et al. (1994), Mortvedt (1994), Sheppard & Thibault (1984), Moffett & Tellier (1977)]. The retention capacity varies with the plant type, the plant tissues (e.g. roots versus leaves), or ore waste type. The uptake can proceed until a depletion concentration has been obtained, the magnitude of which differs depending on element and occasion.

As a rule, concentration of natural uranium and thorium in plants growing in soil near uranium mining is higher than in plants growing in background soil. In 2004 we had shown that fir- trees that grown up on the mining dumps from Crucea U-ore deposit represent a good concentrator for uranium [Petrescu & Bilal (2003)]. In the present paper, we give additional data for the U, Th and Sr transfer to conifers grown within a uranium ore deposit. We also study the relationship between U and Th and the essential elements Ca and P searching for analogies with essential elements for plants. The bioaccumulation of U, Th and Sr in the conifers resulted in the removal of these metals from the soil and reduces the risk to the environment.

2. GEOLOGICAL BACKGROUND

The host rocks belong to the crystalline-mesozoic zone in the northern part of the East Carpathians. Petrescu (2004) gives additional details concerning the geology and mining operation in the area.

U-mineralization is confined to the brecciated retrometamorphic micaschists, invading by carbonates and clay minerals. The richest uranium mineralization is associated with four NW-SE faults with E or W strike. Primary mineralization consists of pitchblende included in bitumen. An intimate association between pitchblende and bitumen characterizes this U-ore deposit. The content of sulfides is lower than 10% and consist of pyrite, marcasite, chalcopyrite, and minor galena, sphalerite, arsenopyrite and tetrahedrite. Carbonates form the gangue.

The geochemical background of uranium in the surrounding area is lower than 3 ppm, whereas in the mining area it reaches 5.39 ppm in the waste rocks and 7.26 ppm in soils [Petrescu & Bilal (2003)].

The exploration and exploitation facilities include 31 galleries, situated between 780 and 1040 m above sea level. Radioactive waste resulted from mining are disposed next to the mining facilities. The waste rock was disposed in piles of variable sizes that are spread over an area of 364,000 m^2. Older dumps (18) have been already naturally reclaimed by forest vegetation, which played an important role in stabilizing the waste dump cover and in slowing down the uranium migration processes.

The mining waste-vegetation cover is characterized by coniferous species, consisting of *Abies alba, Picea excelsa* and *Larix decidna* and deciduous tree such as *Carpinus betulus*, *Acer negundo* and *Fraxinus excelsior*. The undergrowth consists of shrubs, such as *Vaccinium myrtillus* and *Rubus idaeus*, and different forest species from spontaneous flora, such as *Dryopteris filix-mas*, *Lipidium draba*, *Holoshoenus vulgaris*, *Urtica dioica, Xanthium spinosum* and grass [nomenclature follows Tutin et al. (1993)].

3. ANALYTICAL METHODS

Samples were collected in June 2004 from different mining wastes in the Crucea uranium deposit (Bistrita Mountains, East Carpathians), mainly from 1, 4, 5, 6, 8, 9, 1/30 and 950 mining dump galleries (*fig.1*). Conifers samples and afferent soils were taken at each mining site. Twenty-six soil samples; twelve fir-trees and eight spruces have been collected from the mining dumps. The ages of the conifers were 3-5 years.

Soil samples were collected both from the upper part and from the slope at each mining dump as well as from the plant root zones. Samples were collected with a 7.5 cm (3 in.) diameter stainless steel auger from a depth of approximately 15 cm (5 in.). Cross contamination during sample collection were minimized using disposable gloves that were replaced after each sample. The samples were stored at room temperature in Ziploc® bags. The samples were air-dried at 25ºC for three days and then dray-sieved at 2 mm to remove the large clasts, vegetation and litter and the fraction less 2 mm was used. These 2 mm fractions were than milled in an agate pot to pass a 100 μm sieve.

For some toxic heavy metals (U, Th, Cu, Ni, Pb, Zn) the sequential extraction, as it can be postulated by Tessier et al. (1979), cannot be always successfully applied in order to achieve the correlation with the quantities absorbed by the plants. The EDTA extractable fraction is considered to be an estimation of the non silicate-bound metal fractions of the soil available for being retained by the vegetation, both on short and relatively long term [Lo & Yang (1999), Ure (1996)]. The trace elements that could become available for vegetation roots have been determined by Inductively Coupled Plasma – Optic Emission Spectroscopy (ICP-OES), using extraction with ethylenediaminetetraacetate (EDTA). A HORIBA Activa Jobin Yvone system was used.

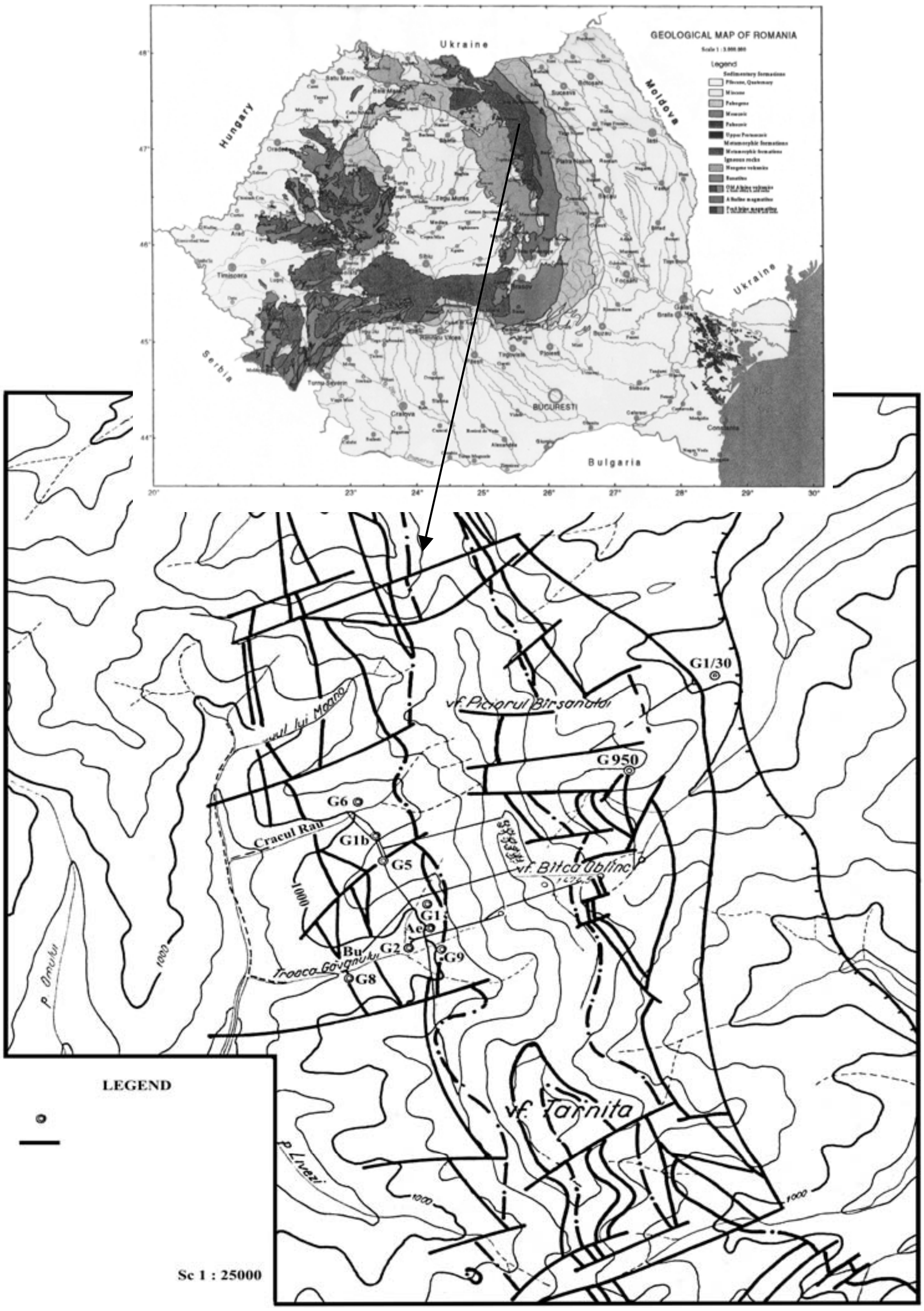


Fig.1. Topographic map of the investigated area with the sampling points.

We have used the method of extraction in one step developed by Lo & Yang (1999). The extraction was carried out on an initial weight of 1.00 g of sample in 50 mL Nalgene® polypropylene centrifuge tubes to facilitate centrifuge of the soil. The soil was treated with 0.5 mol·dm^{-3} disodium EDTA dihydrate $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ (adjusted to pH 7.0), shaken in an end-over-end shaker (at a speed of 180 rot·min^{-1}) for 30 minutes. The supernatant liquid was removed after centrifugation at 10,000 rot·min^{-1} for 15 minutes and diluted to volume. An initial soil to reagent ratio of 1 g : 20 mL was used. Extractant solutions were analyzed for U, Th and Sr. The results were corrected with control samples of the same matrix. The controls were passed through the ICP at the same time as the sample.

Sub-samples of untreated soils were analyzed by X-Ray Fluorescence Spectroscopy (XRF) using pressed powder pellets. A SRS3400 Bruker AXS was used. The untreated samples provide baseline data for total metal contents.

Conifers samples were collected at the same points at which the soil samples were taken and bagged in paper. Each sample was rinsed in deionised water to remove adhering soil, then air-dried at 25ºC for several weeks and the plants were separated in different organs, e.g. roots (primary + secondary), stems, twigs and needles.

Before the analysis, the air dried plant material samples were finely grounded in an agate mortar, homogenized and dried at 103 ºC. 1.000 gram of sample was decompose with concentrated nitric acid in Pyrex® pressure bombs at a temperature of 140 ºC and then the concentrations of the elements were determined in clear solution by ICP-OES [Pungor (1995)]. The following elements were determined: U, Th, Sr, Ca, Mg, Mn, Fe, Al, Si, Na, K and P.

A rigorous quality control program was implemented, included analytical-reagent solutions, laboratory standards and deionised water (MILLI-Q system, conductivity < 18 MΩcm)

The reliability of the chemical analyses was calculated from the four duplicate samples with the analysis of variance proposed by Garrett (1973). The F-ratio, which is a measure of the ratio of total data variance to error variance (sample inhomogeneity, analytical error) and which has to be >4 to be significantly high at the 99% level of confidence, was >1000 for Ca, Mn and Na, >100 for U, Th, Sr, Al, Fe, K, P and Mg and 54 for Si. Hence, any pattern or absence of pattern of any of these elements in the data set is not due to analytical or sampling error.

4. RESULTS AND DISCUSSION

The analytical results for soils samples collected from Crucea ore deposit are given in *tables 1,2*.

The average of total concentrations of U, Th and Sr are given in *table 1.* All the data, average of 4 independent samples, were calculated based on dry weight. The elevated standard deviation of data collected from various sample locations indicated significant spatial heterogeneity in analyte concentrations.

Table 1. Summary of total concentrations of selected elements (ppm) in soils collected in Crucea region.

Variable	Minimum value	Maximum value	Mean value	Standard deviation
U	6.10	680.70	52.48	27.57
Th	7.70	115.30	22.54	21.68
Sr	56.40	162.00	112.34	28.75

In *table 2* is presented the metal concentrations of the EDTA fractions. The bioavailability of the metals from the soil decrease in the following order: Th(21.91%) > U(6.20%) > Sr(3.01%). This proves that some actinides as, for instance Th, are bioavailable for plants, although they are mostly caught in the silicate, organic matter, carbonates and ferromanganese oxy-hydroxides, and the EDTA is a good extractant for these ones. The fact that EDTA removes only 6% of the uranium from the soil proves that the insoluble organic matter absorb irreversibly U. Even if a part of the uranium is immobilized by the insoluble fractions, because the fact that plants can absorb the soluble forms of U, any mechanism increasing the mobility of uranium, including the forming of complexes and association with the colloids, will conduct to a better retention of this element by the roots. On the other hand, it was suggested [Hunsen & Huntington (1969)] that mobility of Th in soil might be less affected by soil pH than by soil organic matter. Th^{4+} may be strongly complexed with soil organic matter, thus increasing the mobility of Th in soil.

Reflecting these results, we were able to prove that the examined mining dumps can represent an impact on the environment, which constitute an argument in favor of the initiation of a program of remedying the quality of the environment from this mining zone.

Table 2. Summary of selected elements from soils (ppm), disponible for vegetation roots.

Variable	Minimum value	Maximum value	Mean value	Standard deviation
U	0.20	8.65	1.72	1.36
Th	3.37	4.03	3.60	0.15
Sr	1.65	6.57	3.20	1.39

We have analyzed the minor and major cation contents from different constituent parts of conifers: needles, twigs, stems, roots (*table 3* and *table 4*), and its relationships with bioavailable heavy and radioactive metal concentrations from soil. The conifers accumulate a great amount of uranium, up to 780 ppm in total plant. The concentration of uranium in the conifers parts collected from mining area ranged from 22.5 ppm to 358.46 ppm, thorium concentration varies between 3.46 ppm and 69.67 ppm and strontium between 22.35 ppm and 398.76 ppm. A coefficient of linear correlation, r = 0.97 (*fig.2*) and r = 0.89 (*fig.3*) was emphasizes between U and Th respective U and Sr. The correlation suggesting that the evergreen trees which assimilate U, can also assimilate Th and Sr.

In the case of fir-trees collected from the proximity of the ore silo (BU sample), we could notice an increase by 236% of the quantity of uranium assimilated by the twigs and by 285% of the quantity of uranium assimilated by the needles – in comparison to the average of the others samples. This increase could be the result of a possible contamination with ore dust in the air.

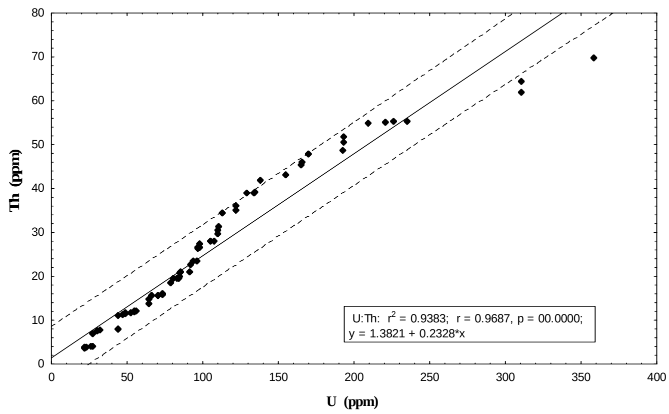


Fig. 2. Variation of U *vs.* Th in conifers collected from mining area ($r = 0.97$).

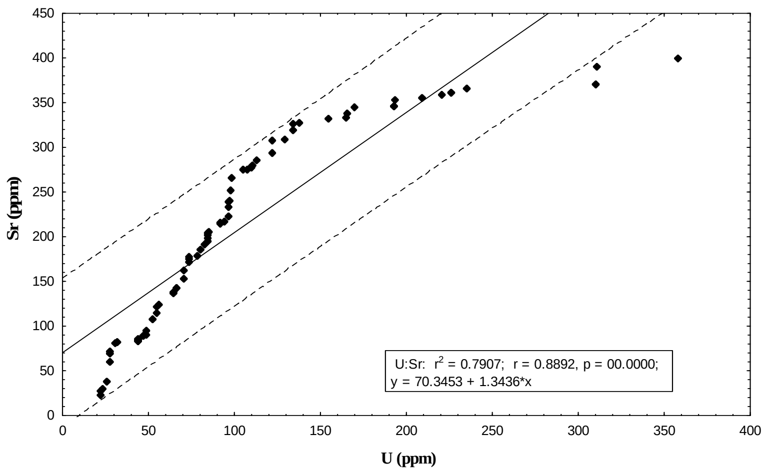


Fig. 3. Variation of U *vs.* Sr in conifers collected from mining area ($r = 0.89$).

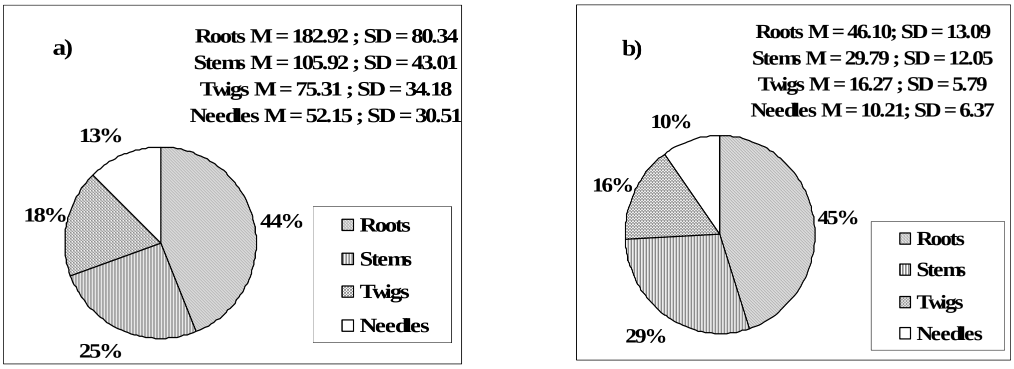
Table 3. The mean (M) and standard deviation (Std) concentrations of major elements (ppm) in conifers grown on mining dumps (n = number of samples).

Species	Tissues		Ca	Al	P	Fe	Si	Mn	Mg	Na	K
Upper part of the mining dump											
Abies alba n = 6	roots	M	1342.83	103.38	16.36	147.42	34.28	20.67	524.00	252.18	1348.17
		Std	333.41	39.43	1.20	44.30	8.86	13.88	166.49	109.11	463.78
	stems	M	2608.17	59.68	6.95	120.77	30.27	20.95	381.17	250.12	1020.67
		Std	463.45	28.25	2.57	47.73	8.41	8.20	64.63	110.71	169.11
	twigs	M	3988.00	89.17	7.30	181.02	35.10	25.78	626.00	244.93	1648.83
		Std	1202.07	47.17	1.13	106.08	7.65	14.16	188.24	108.69	845.26
	needles	M	6561.50	296.73	8.32	478.65	53.50	62.22	745.83	248.93	3099.83
		Std	1901.40	221.98	1.04	221.51	13.99	19.23	241.63	112.96	891.72
Picea excelsa n = 5	roots	M	1004.50	101.85	19.09	138.35	38.80	22.15	651.50	247.00	1130.00
		Std	215.67	63.85	0.83	65.97	6.36	10.68	51.62	45.25	60.81
	stems	M	2447.50	117.10	6.36	217.50	46.10	22.30	548.00	273.50	1080.00
		Std	532.45	29.56	0.72	79.90	20.36	0.00	195.16	95.46	55.15
	twigs	M	4417.00	179.50	7.41	321.50	31.25	28.80	652.00	266.50	1818.00
		Std	1736.65	86.97	0.97	70.00	13.08	14.14	268.70	95.46	18.38
	needles	M	7062.50	215.50	8.60	528.50	43.30	37.65	776.50	263.50	2636.50
		Std	1885.85	62.93	0.92	64.35	22.77	8.70	129.40	86.97	146.37
Slope of the mining dump											
Abies alba n = 6	roots	M	1469.50	92.48	15.01	144.70	33.58	20.85	456.67	212.52	1133.50
		Std	688.50	31.38	2.96	55.11	19.56	10.25	257.54	130.09	329.18
	stems	M	2702.83	45.58	5.29	93.18	26.12	26.77	325.00	221.25	1190.33
		Std	1262.82	17.28	1.02	45.06	6.42	15.05	78.53	141.39	369.82
	twigs	M	4791.17	64.58	6.61	130.60	24.33	25.73	409.67	213.28	1351.00
		Std	1835.95	29.64	1.06	70.18	8.04	19.69	193.93	134.41	606.78
	needles	M	6632.33	305.30	7.78	309.17	56.88	47.35	710.00	211.83	3709.67
		Std	2132.78	283.89	1.18	165.26	27.60	16.01	253.46	129.98	1311.29
Picea excelsa n = 5	roots	M	1247.00	93.93	14.70	153.13	26.93	12.32	400.00	217.90	1071.00
		Std	336.96	89.68	2.53	134.81	10.59	6.34	149.71	110.04	291.88
	stems	M	2520.25	29.63	5.01	50.90	26.30	17.31	296.50	214.73	745.75
		Std	382.28	27.49	1.05	45.90	11.20	9.84	174.99	123.54	446.35
	twigs	M	4971.50	73.68	6.55	136.25	27.60	23.23	490.50	206.75	1454.75
		Std	735.11	39.17	1.60	42.77	6.94	9.36	158.22	113.75	488.21
	needles	M	7361.00	224.05	6.83	282.50	153.20	89.00	860.50	219.33	2892.00
		Std	864.24	193.50	1.39	102.41	102.61	47.09	148.04	116.01	394.53

Table 4. The mean (M) and standard deviation (Std) concentrations of traces elements (ppm) in conifers grown on mining dumps (n = number of samples).

Species	Component parts		Cu	Th	Sr	U	Zn	Pb	Co	Ni	Cr	V
Upper part of the mining dump												
Abies alba n = 6	roots	M	121.01	50.37	164.65	218.45	802.04	128.23	10.94	50.00	37.49	13.77
		Std	33.81	15.14	109.04	76.29	446.56	79.60	5.81	15.06	15.37	5.12
	stems	M	92.99	36.40	187.83	125.85	1185.92	49.17	6.71	34.51	16.63	7.80
		Std	35.29	16.39	112.39	54.19	805.20	21.70	2.51	10.01	7.27	1.87
	twigs	M	112.22	17.87	205.54	74.46	1075.90	38.44	8.95	39.10	10.69	6.30
		Std	20.76	6.23	111.18	34.66	518.35	12.25	5.26	12.89	2.86	1.83
	needles	M	75.76	8.03	238.27	45.30	1101.51	31.20	9.59	37.52	9.35	4.72
		Std	23.84	4.10	124.80	34.14	556.57	12.23	6.13	14.06	2.96	1.04
Picea excelsa n = 5	roots	M	155.63	43.79	192.53	310.86	864.87	231.72	13.97	57.12	40.17	17.95
		Std	4.24	6.92	56.80	0.14	126.83	48.91	14.00	55.21	9.52	1.21
	stems	M	147.77	38.34	221.86	75.73	983.07	68.67	7.15	61.25	21.89	8.19
		Std	87.63	4.78	25.68	12.71	262.95	29.40	5.00	19.61	9.35	4.35
	twigs	M	93.03	18.22	279.67	64.48	1019.42	58.84	21.09	60.77	12.44	7.67
		Std	7.84	3.73	106.76	28.43	22.48	38.18	12.73	35.81	3.28	0.67
	needles	M	102.71	14.30	303.17	50.43	1270.87	51.42	9.31	33.46	9.01	6.46
		Std	25.38	9.23	122.77	8.57	108.08	36.32	1.35	0.27	0.50	1.50
Slope of the mining dump												
Abies alba n = 6	roots	M	114.37	44.42	184.43	134.52	654.87	86.94	8.97	42.82	25.01	13.03
		Std	36.22	10.63	146.25	46.48	449.18	69.18	8.56	15.10	9.53	6.94
	stems	M	82.72	27.44	203.76	103.39	819.12	42.36	4.27	35.13	13.45	6.00
		Std	23.19	4.71	126.50	46.72	466.00	19.82	2.02	12.69	7.10	2.07
	twigs	M	76.29	15.92	188.21	87.72	926.62	32.15	5.63	41.94	9.02	5.10
		Std	42.51	6.71	126.52	45.21	662.82	12.57	1.70	29.69	2.34	1.29
	needles	M	70.30	12.00	180.75	59.81	1146.99	26.29	10.47	35.91	5.20	3.43
		Std	18.66	8.13	118.05	39.40	840.89	14.99	5.45	16.15	2.28	1.26
Picea excelsa n = 5	roots	M	84.61	43.36	123.16	138.24	477.04	113.33	4.79	15.19	15.07	12.40
		Std	46.51	18.13	35.70	49.87	307.26	92.30	2.85	5.01	5.24	4.16
	stems	M	64.80	19.10	178.37	93.10	745.84	46.70	3.17	19.23	11.43	6.86
		Std	29.51	5.59	31.36	16.20	270.60	32.22	1.14	12.45	4.80	2.10
	twigs	M	57.60	13.39	264.24	63.38	926.42	33.62	5.22	34.16	6.74	5.89
		Std	19.45	5.17	18.45	19.14	409.79	16.79	2.04	23.11	3.11	0.90
	needles	M	74.57	6.73	328.42	47.17	1195.12	24.95	13.01	27.26	4.58	4.03
		Std	8.60	5.90	39.37	17.88	428.34	11.20	9.48	19.80	2.12	1.42

The concentrations of uranium in the tissues of the conifers decreases in the following order: roots >> stems > twigs > needles (*fig.4.a*). Thus, the roots of the conifers act as a powerful retained mechanism, collecting the U from a large enough volume of soil. Although most of the uranium is precipitated in the roots'cells, relatively high quantities reach the upper part of the plants and are deposited in these parts. This comes in accordance to the discoveries of others researchers [Sheppard & Thibault (1984), Sheppard & Sheppard (1985), Sheppard & Evenden (1988), Sheppard (1989), Popescu et al. (1997)] that emphasize the fact that the uranium is poorly translocated in the upper parts of the conifers and they accumulate especially in the roots. If the conifers should happen to be affected by diseases, the needles are of great importance. The needles concentrate > 10% of the total quantity of assimilated U and Th respectively >30% of assimilated Sr, and at decomposition of leaf litter the reincorporation of those elements into the soil is faster.



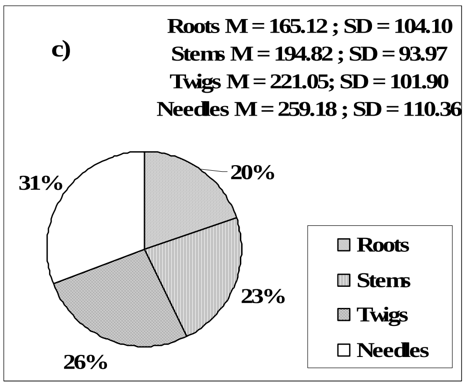


Fig.4. Distribution of U (a), Th (b) and Sr (c) between the vegetal tissues of conifers; (M = mean, ppm; SD = standard deviation, ppm).

For the behavior of Th and Sr, we noticed that the first concentrate mainly in the roots, that is just like in the case of U (*fig.4.b*). This is a rather common phenomenon. Roots serve as a specific natural barrier preventing penetration of toxic elements into upper parts of plants. Sr has a different behavior. In conifers Sr is found to be preferentially concentrated in needles and twigs than in roots and stems (*fig.4.c*).

The assimilation of the U by the conifers depends also on their position on the mining dump – on his upper part or on its slop (*fig.5*). We have determined an obviously higher concentration of the uranium in the conifer's roots growing on the upper part of the waste. This is the result of a probable longer contact with the streaming waters.

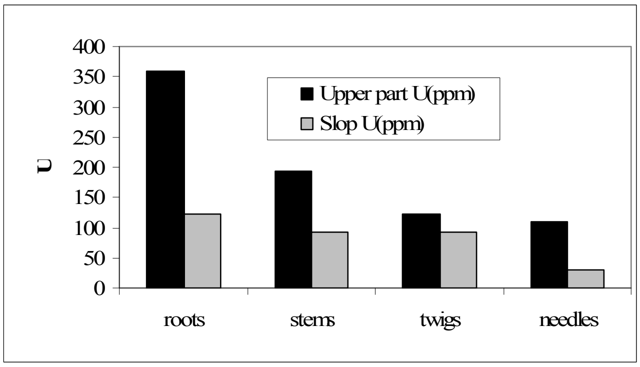


Fig.5. Assimilation of the uranium influenced by the position of the conifers on the mining dump (in the case of fir-trees grown-up to G5bis mining dump).

The soil-to-plant accumulation factor (AF) is frequently used to describe the transport between the soil and the plant components. It may be defined as the ratio plant (dry wt.) to soil (dry wt.) heavy metals (*Me*):

$$AF = \frac{M_e \text{ in plant}}{M_e \text{ from the soil available for the plant's roots}}$$ [Kabata-Pendias & Pendias (2001)].

The AF index is a measure of the plants capacity of absorbing these metals from the soil. We have used the quantity of metals available for being assimilated by the plants, instead of the total quantity of metals from the soil, because the first one is much closer to the reality for a reasonable time period and for reasonable geochemical conditions. Some researchers [Punshon et al. (2003), Ure (1996)] also recommend the use of the metals quantity available for being assimilated by the roots. The soil-to-plant AF was calculated according to the presumption that the entire system of roots was subject to the contaminated soil.

Table 5 shows the AF index for U, Th and Sr in different parts of conifers. According to the *table 5* the soil-to-plant AF for uranium in conifers is high. We established an index of 210.50 for fir-trees and 170.86 for spruce. According to the conifer's organs, the AF of the uranium varies for these species between 22.25 (in the fir's needles taken from the upper part of the G4 mining gallery dump) and 358.46 (in the roots of the fir-tree collected from the upper part of G5bis mining gallery dump). Therefore, the highest AF appears in the case of the roots, followed at a great distance by the stems, the twigs and the needles (*fig.6*).

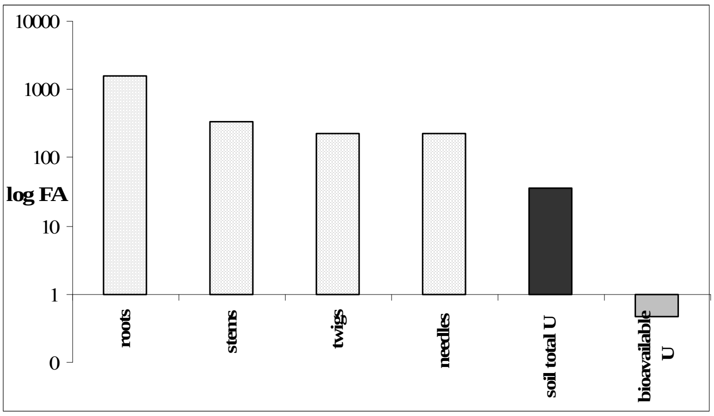


Fig.6. The FA for the vegetal organs of spruce-tree collected from the upper part of G5bis mining dump, in comparison with total U from soil (ppm) and available U from roots (ppm).

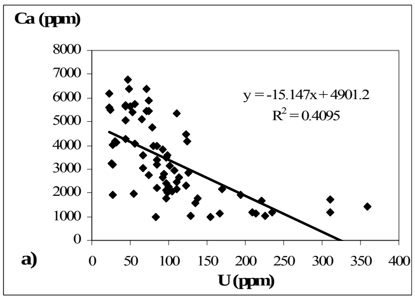
For thorium the AF is low and varies between 3.46 (in the fir's needles taken from the upper part of the G9 mining dump) and 69.67 (in the roots of the fir-tree collected from the upper part of G9 mining dump). The AF for strontium is quite great and varies between 22.35 (in the fir's roots taken from the slope of the G6 mining dump) and 398.76 (in the fir's roots taken from the slope of the G5bis mining dump).

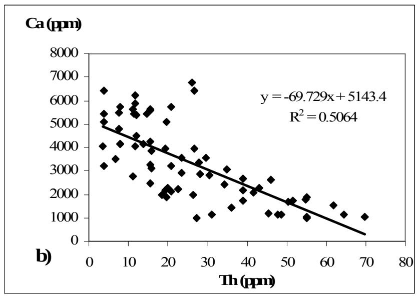
There is no linear correlation between the total U content from the soil and the AF of the uranium from the vegetation. This result could contradict the opinion of some researchers [Mortvedt (1994)] who state the existence of a constant relation between the concentration of the U from the soil and the concentration of the same element from the plants. This may be explained by the fact that the variation of a stable element in the plants cannot fluctuate around a constant value because it depends also on some others variables from the environment. The linear correlation can only be applied in the case of plants that do not grow on the soils affected by the anthropic activity or to the water-grown plants. If the U from the soil results from a recent contamination, this implies a high availability of this element in the environment, which was also indicated by Blanco Rodriguez et al. (2002). An increase of the U, Th and Sr concentration in the soil will lead to an increase of these elements in the fractions available for the plants.

Table 5. The AF index for U, Th and Sr in different tissues of conifers.

Location	Plant species / tissues	U	Th	Sr	Location	Plant species / tissues	U	Th	Sr
G1bis	Fir – roots	235.27	64.34	121.07	G8	Spruce – roots	310.76	48.68	152.37
upper part	Fir – stem	94.34	30.35	194.35	upper part	Spruce – stem	84.72	41.72	203.7
of the	Fir – twigs	70.77	11.4	332.62		Spruce – twigs	84.58	20.86	204.18
mining dump	Fir – needles	23.63	7.59	370.11		Spruce – needles	56.49	20.82	216.36
G1bis	Fir – roots	113.33	45.94	200.73	G8	Spruce – roots	209.59	45.34	141.76
slope	Fir – stem	84.87	26.56	277.5	slope	Spruce – stem	105.14	22.58	185.26
	Fir – twigs	70.77	26.56	345.54		Spruce – twigs	78.93	7.55	274.17
	Fir – needles	47.17	26.21	351.79		Spruce – needles	52.64	3.78	358.09
G4	Fir – roots	169.81	38.96	250.76	G9	Fir – roots	226.26	69.67	80.85
upper part	Fir – stem	66.62	23.31	293.35	upper part	Fir – stem	193.32	55.23	80.94
	Fir – twigs	44.36	19.66	331.69		Fir – twigs	84.9	27.85	83.78
	Fir – needles	22.25	11.67	365.27		Fir – needles	55.38	3.46	94.24
G5	Spruce – roots	310.96	38.9	232.69	G9	Fir – roots	138.24	51.72	285.05
upper part	Spruce – stem	66.74	34.97	240.02	slope	Fir – stem	98.42	29.56	307.83
	Spruce – twigs	44.38	15.58	355.16		Fir – twigs	73.86	14.77	327.03
	Spruce – needles	44.37	7.77	389.99		Fir – needles	73.88	11.6	325.4
G5	Spruce – roots	110.79	47.79	162.1	AE	Spruce – roots	98.24	18.44	106.73
slope	Spruce – stem	85.61	19.4	176.67	slope	Spruce – stem	73.84	11.1	213.75
	Spruce – twigs	44.48	15.59	238.02		Spruce – twigs	49.33	11.06	279.54
	Spruce – needles	22.26	15.58	276.93		Spruce – needles	49.16	3.69	360.32
G5bis	Fir – roots	358.46	42.94	343.79	BU	Fir – roots	221.13	50.46	170.68
upper part	Fir – stem	193.4	39.02	345.29	environs	Fir – stem	193.06	19.83	190.28
	Fir – twigs	122.3	15.93	222.38		Fir – twigs	165.44	15.86	136.48
	Fir – needles	110.47	7.79	307.02		Fir – needles	134.59	7.95	274.5
G5bis	Fir – roots	122.19	36	398.76	G1/30bis	Spruce – roots	134.32	61.86	82.04
slope	Fir – stem	92.13	27.99	336.96	slope	Spruce – stem	107.79	23.32	137.78
	Fir – twigs	91.93	11.94	197.18		Spruce – twigs	80.79	19.37	265.22
	Fir – needles	30.7	11.97	214.74		Spruce – needles	64.62	3.88	318.34
G6	Fir – roots	165.92	31.15	68.17	G950	Fir – roots	155.01	55.18	123.27
upper part	Fir – stem	110.25	15.63	70.9	upper part	Fir – stem	97.18	54.89	142.14
	Fir – twigs	27.65	11.72	88.73		Fir – twigs	96.75	20.67	174.07
	Fir – needles	27.67	3.91	114.47		Fir – needles	32.42	13.74	178.51
G6	Fir – roots	82.96	27.38	22.35	G950	Fir – roots	129.26	55	28.98
slope	Fir – stem	55.09	26.47	27	slope	Fir – stem	96.8	34.25	83.01
	Fir – twigs	27.69	19.53	37.5		Fir – twigs	96.6	6.88	85.53
	Fir – needles	26.33	15.56	59.47		Fir – needles	64.72	6.86	89.73

Searching for analogies to essential elements for plants the relations between U / Th / Sr and the major cations Ca and P was studied. Thus, a weak negative correlation was established between the concentration of uranium and that of calcium (r = (–)0.68) (*fig.7.a*). The same negative correlation exists also between thorium and calcium (r = (–)0.75) (*fig.7.b*). Between Sr and Ca we have, this time, a positive correlation (r = 0.64) (*fig.7.c*).





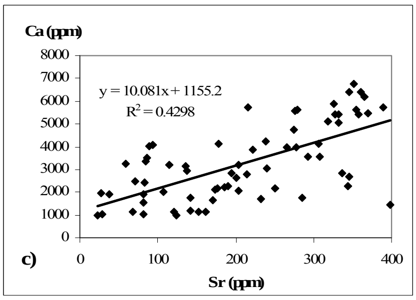


Fig.7. The correlations between U – Ca (a), Th – Ca (b) and Sr – Ca (c) in conifers grown on uranium mining dump.

Ca is an essential nutrient for plants. The element plays an important role in maintaining the integrity and selectivity of plasmatic membranes and is also involved in the growth and functioning of root tips [Fausto da Silva & Williams (1993)]. The diagrams from *fig.7* show that the distribution of the uranium and thorium in conifers is inversely proportional to the calcium quantity, and the absorption of the calcium (which plays an important role in the adjustment of the plasmatic membrane's permeability) are inhibitory for these two elements. An increase of U and Th contents in plants may cause a decrease of concentrations of such essential macro-nutrient as Ca and variation in concentration of many trace elements. The positive correlation between Sr and Ca is the result of the similarity between their chemical behaviors.

A much more tight correlation was determined between U and P (r = 0.78) and between Th and P (r = 0.77), while there is no correlation between Sr and P (r = (–)0.15) (*fig.8*). Blanco Rodriguez et al. (2002) reported similar correlations. The statistically significant and positive correlations between U and P are due to the forming in the roots of the Ca-uranyl phosphates. These uranyl compounds immobilize the U in the roots of the conifers, preventing its translocation towards the upper part of the plants. The forming of the Ca-uranyl phosphates, which are highly insoluble, explains the fact that the U concentrates preferentially in the roots. As a matter of facts, the phosphorus belongs to the class of organogenous elements.

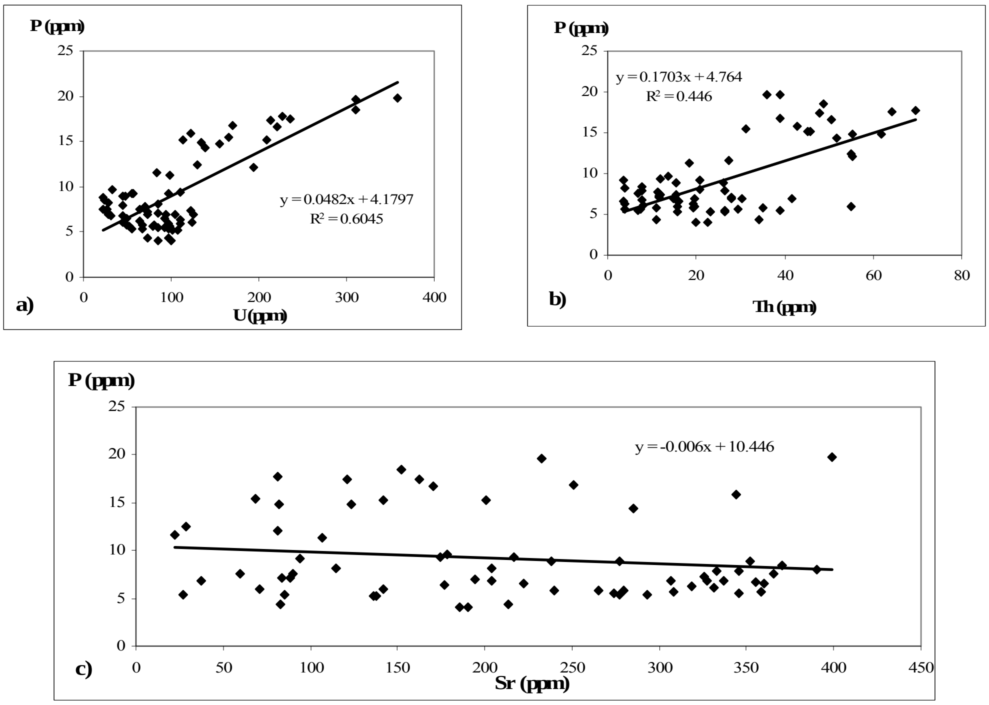


Fig.8. The correlations between U – P (a), Th – P (b) and Sr – P (c) in conifers grown on uranium mining dump.

Although it has been commonly assumed that Th movement through plants tissues is limited by adsorption onto cell walls [Sheppard & Evenden (1988)], in our study there appears to take place specific complexation and chelation processes resulting in increasing mobility and bioavailability of Th. As one can see, a translocation of Th to the upper parts of the conifers was also increased. It is known that cell walls may have a negative charge due to an arrangement of phosphate group of proteins [Fausto da Silva & Williams (1993)]. Thus, owing to the electrostatic attraction between the charged functional groups and organically bound Th^{4+}, the ordinary rate of thorium transport across the lipid membranes of the cells may rise. As the result of the increased membrane permeability, concentration of Th may increase not only in roots, but also in the twigs of conifers.

The availability of Sr is dependent on soil pH and on soil organic matter content. The root uptake of Sr from soil is related to the mechanisms of both mass-flow and exchange diffusion [Elgawhary et al. (1972)]. However, there is more translocation of Sr than of U and Th within the conifers upper tissues.

The low concentrations of U, Th and Sr from the conifers as compared to the high concentration of Ca, Mg, Na, K and Zn (macronutrients and micronutrients, necessary for the development of the plant) (*table 3* and *table 4*) shown that the assimilation of the U and Th is not connected to the physiological needs of the plant.

5. CONCLUSIONS

The increased concentration of U and Th in the surfaced soils is related to dispersion of those elements from wastes. The bioavailability of the metals from the soil (EDTA extraction) decrease in the following order: Th(21,91%) > U(6,20%) > Sr(3,01%).

Increase of U, Th and Sr in soil may lead to enhanced uptake of U, Th and Sr by plants growing in the contaminated soils.

Conifers accumulate natural actinides to different extent. Uptake of U is greater than that Th. One reason for this is that the elements similar to nutrients (such as U and Sr being similar with Ca) follow the same path as the nutrients they are similar to.

The fir *Abies alba* and the spruce *Picea excelsa* were found to have a high uptake capacities of U. The highest concentration was achieved in *Abies alba* roots and twigs. We found that U concentration in plant tissues follow the order: roots >> stems > twigs > needles. Apparently, U is absorbed through the roots system and limited translocation to other plant parts occurs; most U taken up by the conifers remained in the roots.

For the behavior of Th and Sr, we noticed that the first concentrate mainly in the roots, that is just like in the case of U. The levels of thorium concentration in conifers are usually low. We suggested that due to ability of solid phase of soil to absorb Th^{4+} ions, the bioavailability of Th in soils might be rather low. On the other hand, it is known that tetravalent thorium is able to form complexes with organic molecules that roots produce into the rhizosphere; this complexes seem to be more soluble and mobile than the ions themselves. Therefore, the Th-organic complexes may be easily absorbed by roots and translocated to other parts of conifers. Strontium has a different behavior. In conifers Sr is found to be more concentrated in needles and twigs than in roots and stems.

Since the plants do not need U, Th and Sr neither for their metabolism, nor for their structure, it follows that the assimilation of these elements is being done through passive processes (non-metabolic ones). The passive absorption implies the diffusion of uranyl ions and organically bound Th^{4+} from the soils in the endodermis of the roots, do to their imperfect selectivity and increased of permeability of cell membranes. However, there is more translocation of Sr than of U and Th within the plant.

We consider *Abies alba* and *Picea excelsa* behaviors very interesting because they can reach and accumulate U, Th and Sr over very long periods of time. Those plants are tolerant to the radionuclide contamination. It apparently blocked and/or "stored" efficiently the heavy metals particularly in root cells and diminishing the quantity of mobile natural heavy radionuclides. It could be used for the regreening of sites with moderate radioactive / heavy metal pollution. Consequently, planting conifers on U waste slopes may decrease the U, Th and Sr migration.

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