Natural Immobilization of Uranium in Streams

NELSON RODRIGUES[12], JOÃO PRATAS[12], LYS TAVARES[1], ANDRÉ BRANCHES[1]
1 - Earth Sciences Department
Faculty of Sciences and Technology
University of Coimbra
Largo Marquês de Pombal
3000-272 Coimbra
PORTUGAL
nelsonr@dct.uc.pt, https://woc.uc.pt/dct/person/ppgeral.do?idpessoa=8

2 - Geosciences Centre
University of Coimbra
Largo Marquês de Pombal
3000-272 COIMBRA
PORTUGAL

Abstract: - The strategies developed by plants to tolerate heavy metals dictate their survival capability in contaminated places. Sometimes they accumulate significant amounts of those elements. The accumulation ability makes them capable of retaining large amounts of metals thus avoiding the dispersion of these metals and so they become natural cleaners of the environment. This effect is sometimes referred to as *natural attenuation*. However this environmental control is not only due to the vegetation but also to other non-biotic agents such as chemical exchanges with waters, soils and sediments. This work intends to identify what are the principal elements in the ecosystem that are responsible for the immobilisation of uranium coming from the old mine works of Urgeiriça (it was the most important uranium mine of Portugal) and which are dripping into the stream of Pantanha (near Nelas, Viseu, Centre-North of Portugal). It has been verified that the species *Apium nodiflorum*, *Callitriche stagnalis*, and *Amblystegium sp* accumulate large amounts of uranium, as well as the dead leafs and the finer sediments. The uranium concentration in the waters decreases from the discharge point and this concentration drops 30 times in a 3,5 km distance with no human intervention.

Key-words: - Uranium, contamination, ecosystem, Urgeiriça (Portugal), natural remediation, phytoremediation

1. Introduction

Water discharges from industry have been a major source of concern due to potential dispersion of contaminants and consequent health hazards. The discharges, even after treatment, do not always occur in the ideal conditions and the concentrations of toxic elements might fall above the maxima permitted by law. Also accidents do occur that result in unexpected and undesirable input of noxious substances into the environment [1]. However the ecosystems seem to find ways to deal with some of these environmental stresses and they naturally potentiate retention, immobilization and, sometimes, alteration or destruction of the toxic compounds.
For instance clay minerals are known to retain heavy metals, but also the organic matter seems to have a role in controlling the bio-availability and solubilization of metals and metalloids in the environment [2] [3]. This process is often referred to as natural attenuation [4].

Plants that grow in the neighbourhood of mining areas show high tolerance to heavy metals present in the soils and waters and they might even accumulate these metals and, as a result, they can be used in environmental passive remediation techniques – phytoremediation [5], [6], [7].

The objective of this work is to verify the influence of the ecosystem elements on the depuration of uranium contaminated effluents and to measure the distance from source to the point where concentration values have drop to values below maximum allowed limits. A complementary objective is to extrapolate to groundwater protection

zones based on the behaviour of the vegetation of these areas.

The study area is located near Urgeiriça mine, next to Canas de Senhorim (Nelas, Viseu, Centre of Portugal) (Figure 1). This mine is located in the uraniferous region of Beiras.

The uraniferous area occupies about 10000 km^2 and it is contained in the geotectonical Central-Iberian Zone. In this region there are large occurrences of several phases of hercynian granites which intrude the formations of the Ante-Ordovician Schist-Graywake Complex. Above this Complex sits discordantly Ordovician formations. In the region there are also occurrences of Terciary deposits. The uraniferous deposits are located on the hercynian granites, on the metasediments enclaves and in the metamorphism contact haloes.

The principal uranium minerals present in these deposits are pechblende, autonite, thorbernite, uranocircite and sabugalite within quartziferous gang or argyles [8].

Several of these deposits were exploited either by underground or surface mining methods. The main mineral processing method used was lixiviation, in particular during the last working activity phase (the last mine closed in 2001). Many of the places were left in different stages of degradation.

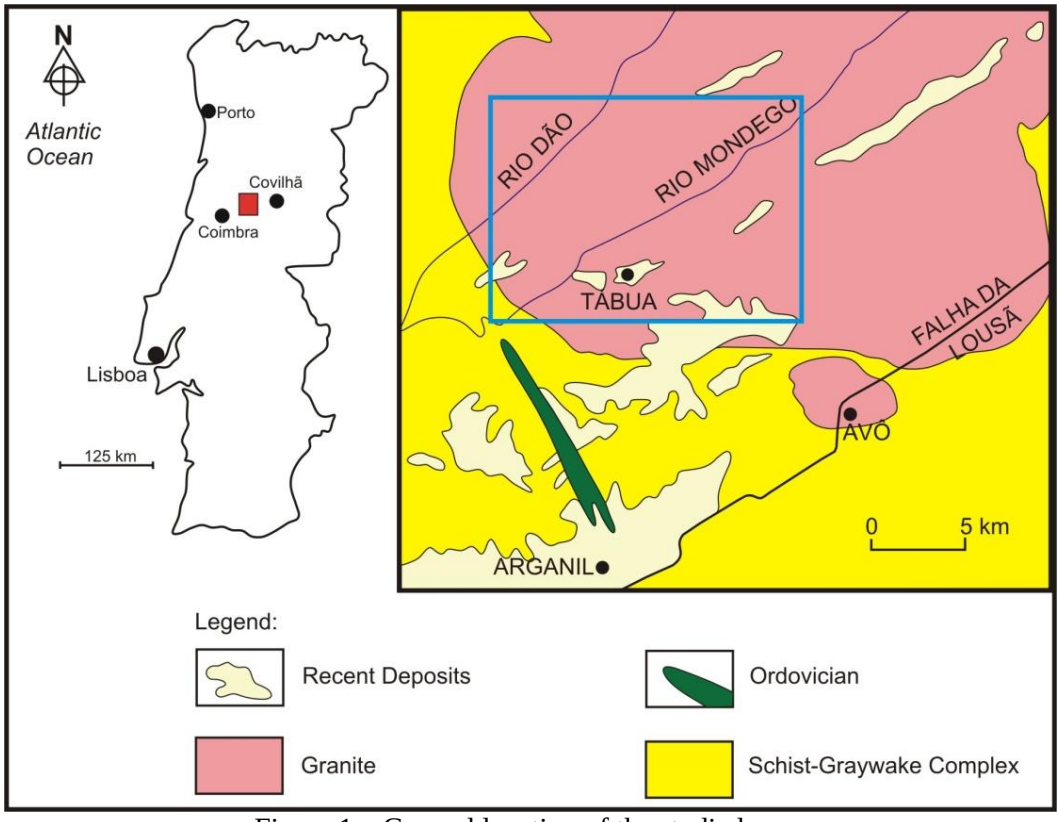

Figure 1 – General location of the studied area.

In the case of the main Urgeiriça mine it was recently rehabilitated, the main tailings have been covered and major remediation work took place in recent years (2005-08, details, in Portuguese, at the following link http://www.edm.pt/html/proj_urgbarvelha.htm).

However a discharge point from there has been left and it feeds into a local stream. This stream is known as *Ribeira da Pantanha*, and the segment of it under observation starts at the mine discharge point and it ends at a point near the confluence with the major river – the Mondego River. This segment is represented in figure 2.

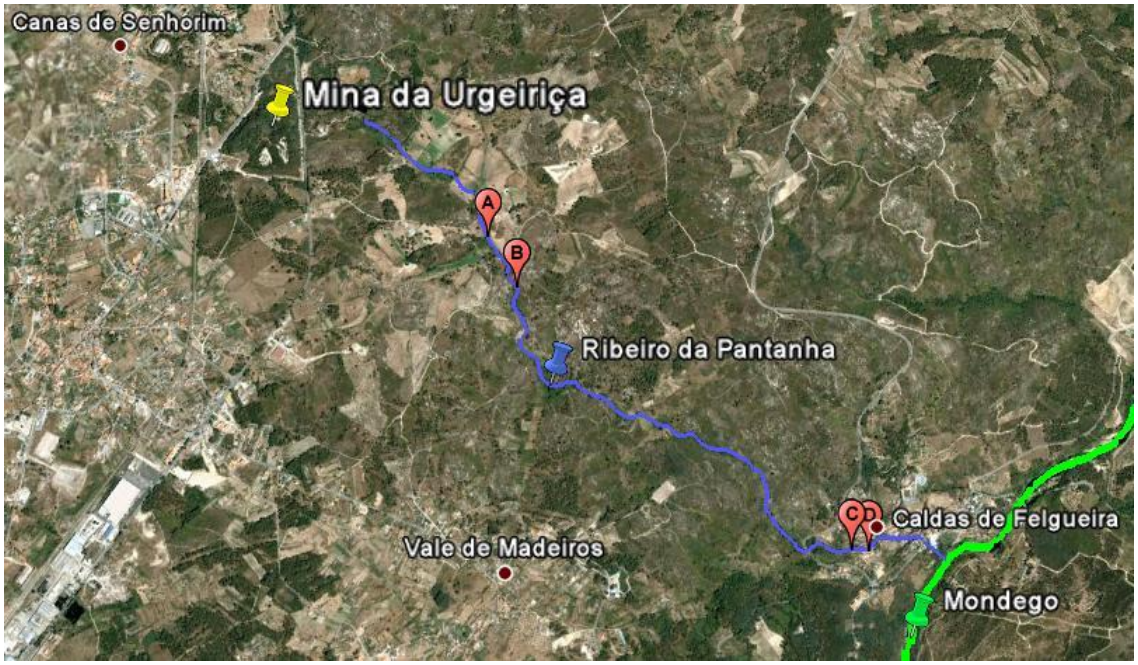

Figure 2: Study area with the Pantanha stream (*Ribeira da Pantanha*), Mondego River and the sampling points A, B, C and D (Adapted from Google Earth, 2010).

2. Methodology

For the evaluation of the segment of the ecosystem affected by the discharge from the old mining area, four points have been chosen for sampling the stream. In each sampling point, all the materials that could somehow participate in the immobilization of the uranium have been collected.

In previous works, the diminishing concentration of uranium from the entry point into the stream and further down in the river had been observed [9], [10], [11] and [12], but the responsible factors for this decrease had not been studied.

2.1. Sample collection

In each point, samples of water, sediment, leafs and all kinds of plants found in the stream bed were taken. The main trees and shrubs of the area have also been analysed to check if they had a role in immobilizing uranium. The sampling points have been designated A, B, C and D, and they have the following co-ordinates: A (40°30'8.84"N, 7°52'51.76"W), B (40°30'1.03"N, 7°52'48.21"W), C (40°29'18.06"N, 7°51'57.70"W) e D (40°29'17.64"N, 7°51'55.90"W).

The sampled macrophyte species were: *Callitriche stagnalis, Apium nodiflorum, Typha latifolia, Spyrogira sp.* (alga), *Polygonum hydropiper* and *Amblystegium sp.*(moss). The trees and shrubs surrounding the stream were sampled where greater diversity was found and where the contamination still is significant (near point B). Here branches have been sampled (leaves and tender stem) of *Quercus robur, Salix atrocinerea, Rubus ulmifolius, Sambucus nigra* and *Acacia dealbata.* The leaves were observed to identify the dominant species in each case, and a great heterogeneity was recorded due to the great diversity in the vicinity of the stream. As a result in points A and B the samples were made mostly of alder leaves (*Alnus glutinosa*). In point C, the dominant species was poplar (*Populus nigra*), whereas in point D the leaves are almost exclusively of *Salix babylonica*.

2.2. Sample analysis

The methodology used for the analysis follows what is described in [13] and the recommendations of the analytical equipment used. Three different procedures have been used: (i) for the vegetable material (including the dead leafs), (ii) for the sediments, and (iii) for the waters sampled.

2.2.1. Vegetable material

The vegetable material was dried in the oven at 60 ^{o}C for a period of 24 hours. Then it was ground and it was homogenized for picking a gram of each ample. This portion was then incinerated at 450 ^{o}C and then it was dissolved in an 8 ml solution of nitric acid saturated with aluminum nitrate. This chemical attack was made in a heated bath for one hour. After mixing and left to cool it was added 10 ml of ethyl acetate, then agitated and centrifuged.

From the supernatant (which corresponds to the organic phase) a 5 ml sample was removed to a porcelain cup and the organic phase was destroyed by burning it in a hot. The remaining residue was dissolved with 7ml of acidified water (HNO3 at 0.005%) and, after that, it was analysed by using the methodology that is described for waters further down.

2.2.2. Sediments

The sediments, after being dried in the oven for 24 hours at a temperature of 60 ^{o}C, were classified for obtaining three fractions: one thicker with a caliber larger than 1 mm, one intermediate between 1mm and 0.180mm and one finer below 0.180 mm. Each fraction was considered and independent sample in order to assess which fractions was accumulating more uranium. The samples, after this procedure, followed the same methodology described for the vegetable material and the chemical analysis was the same as described below for the waters.

2.2.2. Waters

The samples of water were filtered and acidified in relation of 3 ml of HNO3 65% per liter of water for later analysis.

For the analysis of the uranium concentration in the waters and liquors from the other materials (vegetable material and sediments) it was used a fluorimeter (Fluorat 02-2M by Lumex. The concentration of uranium, in this case, is calculated from the intensity of the fluorescence induced by the uranyl ions (λ=530nm) after being excited by ultraviolet radiation.

A standard curve was used which was built with 0 ppb, 2 ppb, 10 ppb 100 ppb and 1000 ppb standard solutions. These solutions are prepared from a 1000 ppb U standard solution. The samples and the standards have been prepared as follows: a) add to a polyethylene cup 5ml of by-distilled water, 0.5 ml of sample or standard and 0.5 ml of polysilicate. The sample is the put in a optic quartz cell and the excitation response is measured in the fluorimeter from which is calculated the concentration.

For quality control of the chemical analysis, certified reference material has also been analysed: Virginia tobacco leaves, CTA-VTL-2, Polish Certified Reference Material and TMDA-62 of the "National Water Research Institute of Canada".

3. Results and Discussion

Table 1 summarizes the results of uranium content in the waters and aquatic plants of the sampled points. From the analysis of the results what stands most is the reduction of the concentration of the uranium in the water in the direction of the flow (figure 3). The reduction is significant because the values drop from an initial value which is 15 times the maximum recommended by EPA for waters for human consumption (30μg /L) [14] to values which are half that maximum. It must to be referred that in the analysed segment of the stream there are no other inputs of water.

The main objective of this study was to analyse the factors that could be responsible for this reduction. In previous works we had already observed this behaviour [10] and [11] but we had not tried to find explanations for it. In those works we had already identified *Callitriche stagnalis* as an uranium hyperaccumulator plant. In the present study we focused on: (1) aquatic plants, (2) dead leafs, (3) sediments and (4) riparian flora.

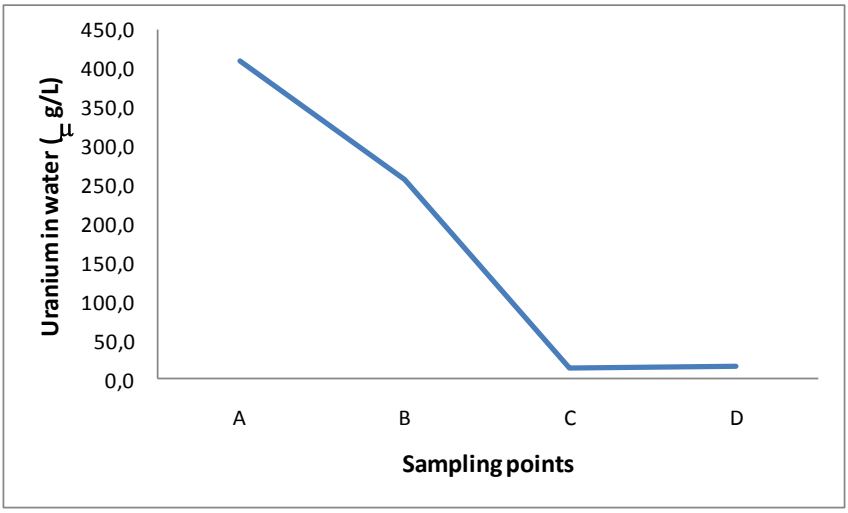

Figure 3 – Uranium content in water of Ribeira da Pantanha.

3.1. Aquatic plants

From the results of table 1 we built the graph of figure 7 where the variation of uranium content in different aquatic macrophyte species is depicted.
In accordance with previous works it can be seen a great accumulation of uranium in *Callitriche stagnalis* (water-starwort, figure 4) particularly in point (A) which is nearest to the discharge point. This reflects the great accumulation potential of this plant species and a lower accumulation downstream where there is less uranium. The fact that there is no intermediate sampling (point B) results from the fact that this plant was not found there probably because this is a point with large slope which makes plant fixing difficult.

Figure 4 – *Callitriche stagnalis* – Best U accumulator of the study.

From this graph it also stands the good accumulation potential of the bryophyte *Amblystegium* sp., which was not found in point A but it shows higher accumulation values in points B and C (closer to the discharge point).
The species *Typha latifolia* (reed mace or broadleaf cattail – figure 5) shows little accumulation of uranium, as it had been observed for other elements [15].This species has an important role in retaining fine material in its thick root system but it is not an accumulator of metals. It is an important plant for a constructed wetland [16], [17] due to the filtering process that it promotes but it does not remove any of the dissolved elements, a fact that is often forgotten in current commercial systems [16], [17].
The *Apium nodiflorum* (fool's water-cress – figure 6) shows constant values (around 130 mg per kg of dried weight) which seems to suggest that it has physiological barriers that prevent the accumulation above a certain level.
The algae of the gender *Spyrogira*, found in this stream, also retain uranium in relatively high concentrations.

Figure 5 - *Typha latifolia* - Good for filtering but not a good accumulator

Figure 6 – *Apium nodiflorum* – Good accumulator

Samples	Sampling points			
	A	B	C	D
Water (μg/L)	409,3	258,0	15,2	15,5
Aquatic macrophytes (mg/kg)				
Callitriche stagnalis	1435,8	-	107,4	110,9
Apium nodiflorum	134,0	-	131,3	130,1
Typha latifolia (leaves)	26,1	-	-	-
Typha latifolia (roots)	53,2	-	-	-
Polygonum hydropiper	-	-	-	95,0
Amblystegium sp.	-	502,9	378,7	199,1
Spyrogira sp.	214,7	228,6	-	138,3

Table 1. Uranium content in the waters and aquatic macrophytes of the sampled points.

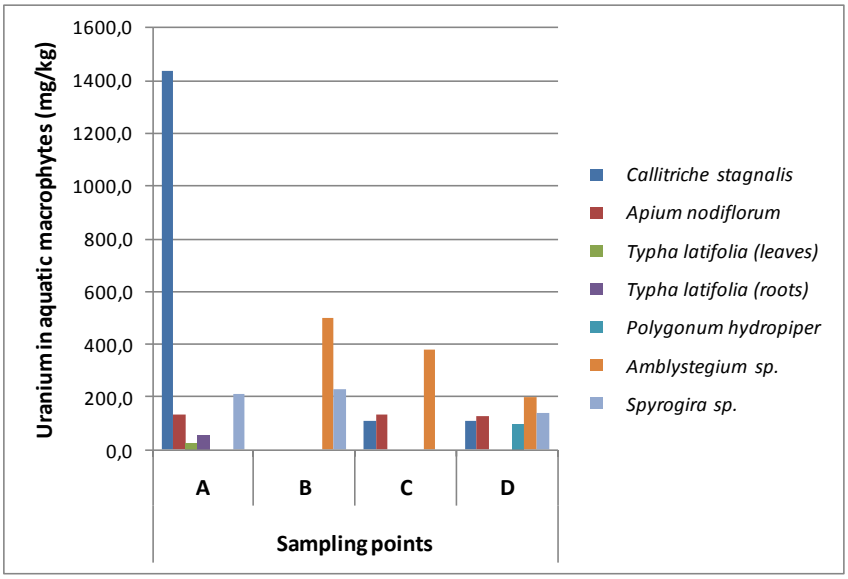

Figure 7 – Uranium content in several aquatic macrophytes sampled in Ribeira da Pantanha.

3.2. Dead Leafs

Observing now the variation in the uranium content of the dead leaves found in the stream bed (Table 2 and figure 8) it can be seen a reduction in the concentration by going downstream except in the last point (D) where the concentration increases significantly.

This could be seen as contradictory but, in fact, this can be explained because, as mentioned previously, the composition of the dead is heterogeneous. In the first two points (A and B), a similar composition was found and it was almost exclusively made of *Alnus glutinosa*. In the third point (C) there was also a lot of *Populus nigra*. In the last point (D), the dead leafs found were almost exclusively from *Salix babylonica*.

The observed results confirm the high ability of accumulation and retention of uranium of dead vegetable material [for instance 17] but this ability is related to the origin of the material: leafs from different species show different responses.

Samples	Sampling points			
	A	B	C	D
Water (μg/L)	409,3	258,0	15,2	15,5
Dead leaves (mg/kg)	111,4	61,3	26,9	159,5

Table 2 – Uranium content in waters and dead leafs found in the stream bed of the sampled points. Results expressed in mg/kg (DW).

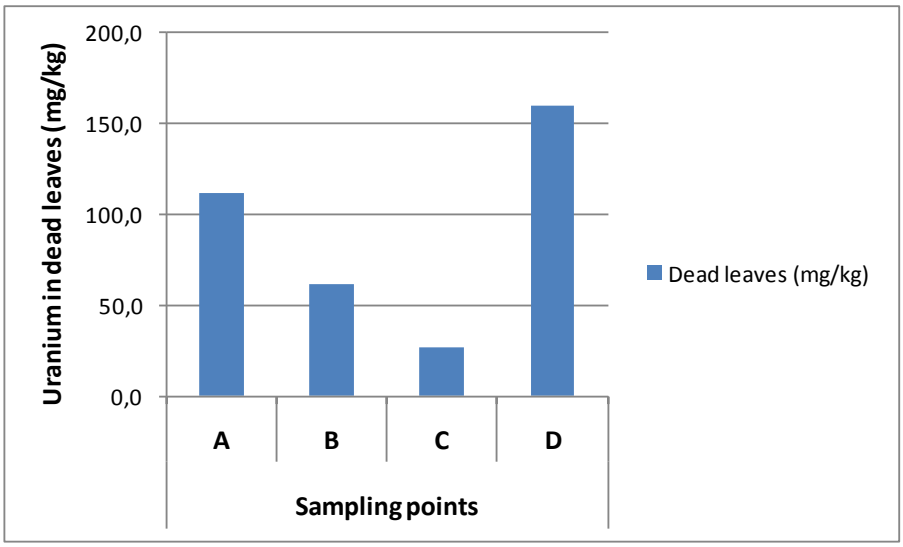

Figure 8 – Uranium content in dead foliage within in the stream bed.

3.3. Sediments

To conclude the analysis of the main elements that might immobilize the uranium in a segment of a natural ecosystem, the sediments have been analysed. Three size fractions were selected to represent the material: a clay and silt fractions which are normally analysed in soils [19], an intermediate sand fraction and a thicker fraction composed almost entirely by quartz. Table 3 and Figure 9 show the variation of the uranium concentration on the sediments.

It can be seen a decrease in the concentration by going downstream after the discharge point. In addition, it can be observed that the finer fractions accumulate more uranium. This can be explained because the finer fractions have a larger surface area and also because the clay material has greater ability for ionic exchange thus justifying the higher uranium content found there.

Samples	Sampling points			
	A	B	C	D
Water (μg/L)	409,3	258,0	15,2	15,5
Sediments (mg/kg)				
< 0,180mm	119,6	94,3	60,6	67,1
1 - 0,180mm	34,2	34,2	37,7	36,1
> 1 mm	9,3	10,9	7,6	20,1

Table 3 – Uranium content in waters and sediments of the stream bed of the sampled points.

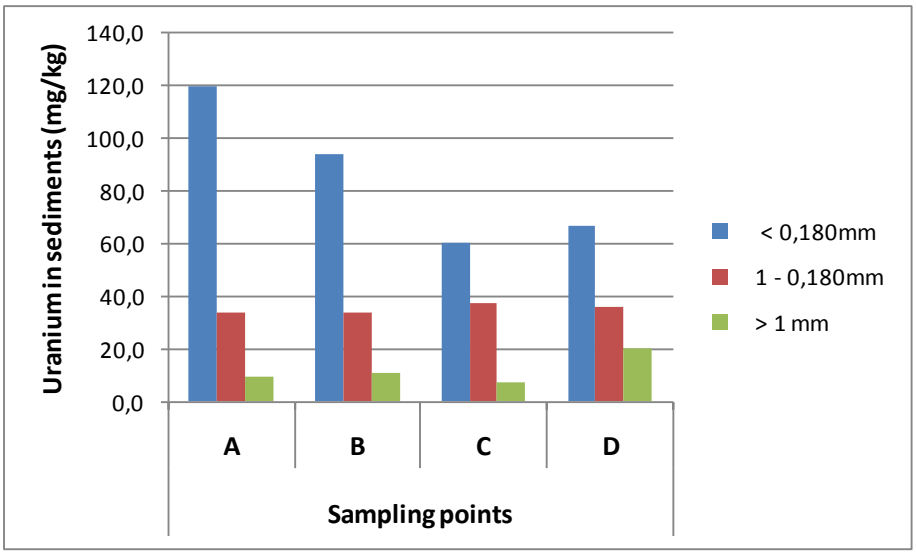

Figure 9 – Uranium content in sediments.

3.4. Riparian flora

In what concerns trees and shrubs that have been sampled near the stream corridor it was observed a small accumulation varying from 0,4 ppm in *Acacia dealbata* to 3.5 ppm in *Rubus ulmifolius*.

These values seem to indicate that they do not seem to contribute much to the immobilization of uranium (Table 4). However these species may contribute indirectly because they are the sources of dead leafs found in the stream bed.

Samples	Sampling points			
	A	B	C	D
Water (μg/L)	409,3	258,0	15,2	15,5
Riparian flora (mg/kg)				
Acacia dealbata		0,4		
Alnus glutinosa		1,9		
Quercus robur		1,2		
Rubus ulmifolius		3,5		
Salix atrocinerea		0,8		
Sambucus nigra		2,9		

Table 4 – Uranium content in waters and riparian flora next to the sampled points.

4. Conclusions

The uranium concentrations measured reinforce our previous studies that claim the potential of the species described here as having phytoremediation potential of mine effluents of radionuclide containing ore. Other authors ([6],[20], [21]) have pointed that there are several species with the potential to accumulate uranium in their tissues. However it seems that a good management of the ecosystem might result in the absorption of the environmental impacts generated by the mining industry [22].

This study shows that several are the materials that are able to retain dissolved uranium originating from mine wastes. It has been shown that in a relatively short path (about 3.5 km) the uranium content has been reduced 30 times compared to the initial values found in the discharging point and this reduction was simply a result of the natural action of the ecosystem.

The uranium got retained by aquatic macrophytes (in particular *Callitriche stagnalis*, the bryophyte *Amblystegium*, the alga *Spyrogira* and the *Apium nodoflorum*). Dead leafs also participate significantly on the retention process but this seems to be linked to the species that produced those leafs.

In the sediments, the uranium appears more in the finer fractions. Clay content and larger surface area are the main retaining mechanisms in this case.

Riparian vegetation found in the vicinity of the stream seems to contribute little to the retention of uranium. However they play an indirect role because they are the sources of the dead leafs found in the stream bed.

An important aspect of the analysis presented here is the fact that the contamination is absorbed by the ecosystem. This process is related to the kind and density of the buffer elements of that particular ecosystem but it is also dependent upon the effluent characteristics.

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