Uranium accumulator plants from the centre of Portugal – their potential to phytoremediation

João Pratas, Nelson Rodrigues, Carlos Paulo

Earth Sciences Department, Faculty of Sciences and Technology of the University of Coimbra, Portugal, carlos.januario@gmail.com

Abstract. The strategies of metal tolerance developed by several plants that enable them to survive in contaminated and polluted sites allow that some of them may accumulate significant concentration of a specific element. The work presented here is part of a larger on going study about the uraniferous geochemical province of Central Portugal, and it focus only in a preliminary description of results obtained with aquatic plants that show potential for phytoremediation. We have observed that *Apium nodiflorum*, *Callitriche stagnalis*, *Lemna minor* and *Fontinalis antipyretica* accumulate significant amounts of uranium, whereas *Oenanthe crocata* inhibit the uranium uptake.

Introduction

The use of plant species as indicators of metal contamination is based on their response to elements present in the substrate (Kabata-Pendias, 2001). Plants growing near abandoned mine sites, usually indicate the mineral composition of the soil and waters. These plant species are tolerant to metals and they are able to accumulate or exclude toxic metals and this ability can be used in mineral prospecting or, if the biomass and bioproductivity are high, in phytoremediation (Hooper and Vitousek, 1997, Brooks, 1998).

The work presented here is part of a larger on going study about the uraniferous geochemical province of Central Portugal. It is oriented for the use of aquatic plants as indicators of metal contaminated waters and their potential use in phytoremediation. Even though we have observed very low concentration of U in the fresh waters of the studied sites we found a set of vegetable species with the ability to accumulate uranium in concentrations which are orders of magnitude higher than the surrounding environment. We have also seen one species that was inhibiting the uptake of this metal.

Location and Geology

The studied area is located in the counties of Tábua, Nelas and Oliveira do Hospital of the Centre of Portugal (Fig.1). This area is in the south-west part of the uraniferous region of Beiras (Centre of Portugal). The uraniferous area occupies about 10000 km^2 and it belongs to 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 discordingly Ordovician formations. In the region there are also occurrences of Terciary deposits.

The uraniferous deposits are located on the hercynian granites, on the meta-sediments enclaves and in the metamorphism contact haloes. The occurrences of uranium define an arch which is located on the NE border of the Serra da Estrela horst.

The principal uranium minerals present in these deposits are pechblende, autonite, thorbernite, uranocircite and sabugalite within quartziferous gang or argyles (Ferreira, 1971).

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

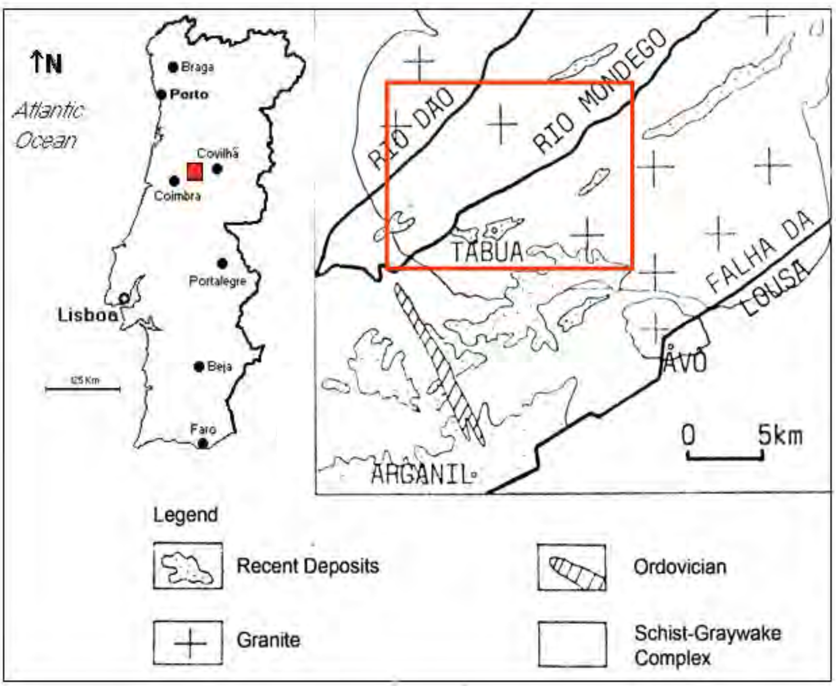

Fig. 1. General location and geology of the study area (Ponte and Pereira, 1991).

Materials and Methods

Field sampling

The samples for this work were collected in running and in standing waters, in the places were it was possible to observe aquatic species. In these sites, samples of the waters and of the vegetable species were taken. The vegetable species collected represented the free floating and the rooted emergent plants in running waters. In the ponds, the collection focused mainly in the free floating plants.

Sampling treatment

All samples were processed in the Chemistry Laboratory of the Earth Science Department of University of Coimbra.

The waters were filtered and acidified. The plants were cleaned in running water in order to withdraw all the residues. Afterwards they were dried in an oven at 60 ºC. After drying, they were ground and crushed for later chemical analysis.

Analytical procedures: uranium determination

For determination of the mass concentration of uranium in samples of natural water and plants it was used the “Fluorat-02-2M” analyzer (made by Lumex, Russia).

In this device the concentration of uranium in solution is deducted from the measurement of the intensity of the delayed fluorescence of the uranyl-ions (λ=530 nm).

The water samples were analysed by standard fluorimetric analysis. For the control of the results it has been used a certified reference water produced by the National Water Research Institute of Canada (reference TMDA-62).

The methodology adopted for the determination of the uranium content in the plants was fluorometry, as described in the work of Huffman, Jr. and Riley, 1970, and Van Loon and Barefoot, 1989). In order to assure the quality of the analytical results certified Virginia tobacco leaves (reference CTA-VTL-2, Polish certified reference material) have also been analysed.

Results

For this preliminary work, we have selected *Apium nodiflorum(L.)Lag.* , *Callitriche stagnalis Scop.*, *Lemna minor L.*, *Fontinalis antipyretica L.* and *Oenanthe crocata L.* among all the collected species because they were the most representative species. A summary of the chemical analysis results is presented in Table 1.

Discussion

The results show a strong accumulation of uranium in the plants in comparison to the uranium present in the water. From these observations we can advocate their use both in biogeochemical prospecting for the location of natural occurrences of uranium or anthropogenic pollution and as an indication of their possible use for phytoremediation of polluted sites.

From the observed species the ones that appear to be more appropriate for phytoremediation are *Callitriche stagnalis* and *Apium nodiflorum*. The first species allows a good rooting in all kinds of running and standing waters and the other species seems to be more appropriate for marginal waters. Their biomass and bioproductivity are relatively high. Both species are also excellent indicators of pollution because they show a large range of values and the results correlate positively with those present in the waters.

The species *Oenanthe crocata,* in spite of its high biomass and bioproductivity, does not reflect, in its aerial organs, a significant accumulation and the values are not correlated with those found in the waters.

The bryophyte *Fontinalis antipyretica* which grows normally on top of the rocks within the waters reveals a strong ability to monitor the contamination present in the running waters.

The free floating *Lemna minor* shows good ability to accumulate uranium in a similar way as it has been observed in *Lemna gibba L.* (Mkandawire and Dudel, 2005). However it was observed a discrepancy when the results from running waters were compared with those from standing waters (Table 2).

Table 1. Uranium Concentration in plant species (expressed in mg/kg DW) and in fresh waters (expressed in ng/mL).

Species	No.of samples	Min	Max	Background	T/t
Apium nodiflorum	10	0,20	31,61	0,31	102
Waters		0,5	18,6		
Callitriche stagnalis	19	0,53	112,16	0,66	170
Waters		0,4	18,6		
Lemna minor	22	0,28	52,98	0,43	123
Waters		0,5	18,6		
Oenanthe crocata	10	0,03	1,68	0,12	14
Waters		0,4	18,6		
Fontinalis antipyretica	10	3,37	32,78	3,83	9
Waters		0,4	18,6		

[a] T/t – relation between the maximum and background level

Table 2 shows that the values of the maximum accumulation, the ratio T/t and the Biological Accumulation Coefficient are much higher in the standing waters compared with those of the running waters. This indicates a positive correlation between concentration in the plant and the residence time for this accumulation. If this is proved to be the case then there is a good opportunity for its use in phytoremediation in closed tanks where it would be grown. This obviously depends on further studies regarding its biomass and bio-productivity.

Table 2. Uranium Concentration in *Lemna Minor* (expressed in mg/kg DW) and in standing and running waters (expressed in ng/mL).

	Samples	Min	Max	Background	T/t	BAC
Plant concentration in running waters	8	0,41	8,54	0,40	21	$1{,}56\times10^{3}$
Waters		0,5	18,6			
Plant concentration in standing waters	14	0,28	52,98	0,45	118	$2{,}87\times10^{3}$
Waters		0,6	4,16			

[a] BAC – Biological Absorption Coefficient

Conclusions

This is a preliminary work envisaging the use of aquatic plants as indicators of metal accumulation and their potential use in phytoremediation. This work focus on waters contaminated by uranium and on the selection of plants which might be candidates for futures phytoremediation studies.

Pursuing these purposes we analysed several representative species of areas we expected to be contaminated with this metal. These areas were old uranium mines where there had been no obvious restoration programs.

This preliminary work opened good perspectives for the use of the selected species in prospecting and in their use phytoremediation.

The species *Fontinalis antipyretica* proved to be a good candidate for biomonitoring. This species accumulates large quantities of uranium in its tissues. It is known that, in general, the bryophytes have a great potential for rapid accumulation and also as good recorders of seasonal fluctuations of the contaminations (Cenci, 2000). Also and due to the fact that this species does not have a root system but only rhizoids the uptake occurs as an ionic exchange between the environment and the leaves with no root intervention. The biological accumulation coefficient for this species is high, of the order of $1{,}4\times10^{4}$, and this means it can be considered an hyperaccumulator plant following the definition of Brooks (1998).

The species *Apium nodiflorum*, *Callitriche stagnalis* and *Lemna minor*, part of the analysed species, also accumulate significant amount of uranium. The species *L. minor* is a floating aquatic plant so the uranium accumulation is only related with the surrounding water concentration. It showed an average biological accumulation coefficient of $1{,}56 \times 10^3$ in running waters and of $2{,}87 \times 10^3$ in standing waters. In both cases there is a great capacity for bioaccumulation and, as before, it can also be considered an hyperaccumulator plant.

These species show great potential for phytoremediation because they are endemic and easy to grow in natural conditions. In addition *A. nodiflorum* and *C. stagnalis* show a good bioproductivity. However it must be stressed that these results are preliminary and further studies are required to properly assess the true potential of these plants for phytoremediation.

Acknowledgements

This work has been funded by a grant of the Portuguese Foundation of Science and Technology (Project POCTI/CTA/41893/2001).

References

Brooks, R.R. (1998), Plants that Hyperaccumulate Heavy Metals, CAB International, 380 p.

Cenci, R.M., (2000) The use of aquatic moss (Fontinalis antipyretica) as monitor of contaminationin standing and running waters: limits and advantages, J. Limnol., 60 (Suppl.1) 53-61.

Ferreira, M. R. P. V., 1971, Jazigos Uraníferos Portugueses Jazigos de Au-Ag-Sulfuretos do Norte de Portugal, I Cong. Hispano-Luso-Americano de Geologia Económica, Lisboa, 81p.

Hooper, D.V., Vitousek, P.M. (1997) The effects of plants composition and diversity on ecosystem processes, Science 277, 1302-1305.

Huffman, Jr. C., Riley, L.B. (1970) The Fluorimetric Method – Its use and precision for determination of uranium in the ash of plants, U.S. Geol. Survey Prof. Paper, 700-B, p 181-183.

Kabata-Pendias, A. (2001) Trace Elements in Soils and Plants, CRC Press, Florida, p. 432

Mkandawire, M.; Dudel, E.G. (2005) Accumulation of arsenic in *Lemna gibba* L. (duckweed) in tailing waters of two abandoned uranium mining sites in Saxony, Germany, Science of the Total Environment, 336, (1-3), 81-89.

Ponte, M.J.B., Pereira, L.C.G. (1991) Aspectos Litológicos e estruturais do complexo xisto-grauváquico no bordo sudoeste da faixa Ordovícica da região de S.Paio-Ázere, Memórias e Notícias, Publ. do Museu e Laboratório Mineralógico e Geológico da Universidade de Coimbra, 12 (A), 135-146.

Van Loon, J.C., Barefoot, R.R. (1989) Analytical Methods for Geochemical Exploration, Academic Press, 344 p.