



# Post-mining water-sediment interaction on U-mine area – a contribution to water management

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## Abstract

The exploitation of uranium mines is responsible for the leaching of toxic elements towards sediments and water, which poses several risks to ecosystems and human health. Sediments have an essential role in contaminant retention processes and are considered a good indicator for water quality. The studied mine site is in Central Portugal. The mine was exploited in an open pit and produced about 12430 kg of uranium oxide (U<sub>3</sub>O<sub>8</sub>), between 1987 and 1988. The mine is abandoned, and the rejected materials were deposited in two dumps and a lake was formed in the open pit. Twenty-one stream sediment and water samples were collected in one hydrological year. The partition coefficient between stream sediments and water suggests that Th has more affinity to be in solution. Otherwise, partition coefficient values for U and for As indicate that these elements tend to be absorbed on stream sediments, which could be suggested by the low variability of U and As water concentrations with increasing distance from mine area. The results suggest that stream sediments could be a water quality indicator and a contribution to water management and future remediation plans in abandoned mine areas.

**Key-words:** Uranium mines, PTE mobility, surface water, sediments, Portugal

## Introduction

The effects of Mining on water resources remain a serious environmental issue, and the main concern is ensuring water availability and quality for different purposes. Water rock-interaction processes are responsible for the transfer of toxic elements to sediments and water at high concentrations. There are about 150 uranium mines in the European Union (Raeva et al. 2014). About sixty mines were mainly exploited in the uranium-bearing granitic rocks from Beiras area (Carvalho et al. 2014), in north and central Portugal, and most of the mine sites are now closed and abandoned. The U-mines have legacies of millions of tons of waste rock and mill tailings (World Nuclear Association 2015). Uranium mines are an important contributor to release of potentially toxic elements (PTE) to water and sediments (e.g. Antunes et al. 2020; 2021; Carvalho et al. 2022), with adverse influence on the environment and

human health. The open-pit lakes associated with abandoned U-mines are responsible for the PTE dispersion to streams and aquifer systems through water-rock interaction processes (Bowell 2002).

Stream sediments in abandoned U-mines play an essential role in contaminant retention processes (Yi et al. 2020; Zheng et al. 2020). Therefore, stream sediments are considered a good indicator for water quality and ecological effects (e.g. Wang et al. 2018; Calmuc et al. 2021; Carvalho et al. 2022). Sediment quality metrics been developed to assess the pollution status and ecological risk of PTE. The geo-accumulation index and contamination factor have been used for ecological risk assessments on abandoned U-mines from Central Portugal (Antunes et al. 2020; Carvalho et al. 2022). The mobility of contaminants in stream sediments could also be estimated using the partitioning coefficient, which determines

the ratio of PTE between solid and dissolved phases at equilibrium (Feng et al. 2017). So, the partitioning coefficient is a relevant contributor to evaluate PTE mobility between water and solid phases in the water-sediment system.

The main objective of this study is to understand the distribution and mobility of U, Th and other PTE concentrations from uranium mine dumps and open-pit lakes to stream sediments and water around an abandoned U-mine site.

### Mine Site Description

The U-mine site is in a small village (Arcozelo da Serra, Central Portugal) and was exploited in an open pit between 1987 and 1988, producing about 12430 kg of uranium oxide (U<sub>3</sub>O<sub>8</sub>). The uranium deposit is associated with quartz veins containing secondary U-phosphate phases, such as autunite and torbernite, associated with a porphyritic coarse-grained two-mica granite.

At present, the mine is abandoned with about 1 million tons of overburden materials deposited in two dumps (fig. 1a), and with a lake formed in the open pit (fig. 1b). The main stream is located downstream the mine dumps and is part of the Mondego River watershed (fig. 1c). Around the old mine, there are several agricultural areas. The abandoned mine and dumps are about 10 m away from the reservoir of the Aguieira Dam on the Mondego River, whose water is used for human consumption and agricultural irrigation.

### Methods

Eleven stream sediment and ten water samples were collected at locations downstream of the open-pit lake and mine

dumps (stream samples CLD1, CLD2, CLD3, CLD4, CLD5, CLD6, CLD7, CLD8, CLD9; water samples CL1, CL2, CL3, CL4, CL8, CL9, CL10, CL14) and outside the area of mine influence (stream samples CLM1, CLM2; water samples CL3, CL5). Samples were collected during one hydrological year. Sediment composite samples were collected up to 20 cm deep from the streambed in the middle of the channel using a scoop or a grab depending on water column depth. Stream samples were dried at 40°C, disaggregated with a silicone hammer and sieved through 2 mm and 250 µm sieves. The pH and electrical conductivity (EC) were measured in a solid-water suspension (liquid/solid ratio of 2.5 and 1/5, respectively) and using the British standard (British Standard 1995a; 1995b). The pH, EC and temperature were measured using a multi-element equipment parameter of Hanna Instruments. Stream sediment samples < 250 µm were digested with aqua regia (3:1 HCl:HNO<sub>3</sub>), filtered through a 2 µm pore size and analysed.

Water samples were collected, and physico-chemical parameters (pH, temperature, EC, redox potential, alkalinity, and total dissolved solids) were measured in the field. Stream sediments and water PTE concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Horiba Jovin Yvon model YV20002 spectrometer with a monochromator at the University of Coimbra (Portugal).

### Results

Most stream sediment samples have a pH value varying from 4.4–6.4 and EC from 13–154 µS cm<sup>-1</sup> and contain low total organic matter (TOM 0.72–5.82 %). Water is near neutral (pH: 6.2–7.2) and poorly

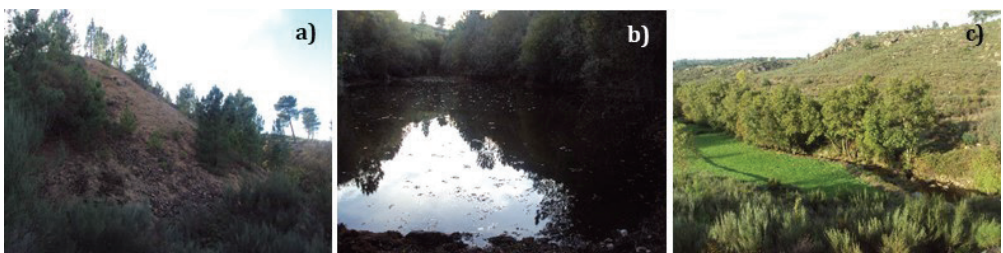


Figure 1 U-mine site: a) dumps and rejected materials; b) open-pit lake; c) stream river

mineralized (EC: 58–111  $\mu\text{S cm}^{-1}$ ; TDS: 32–67  $\text{mg L}^{-1}$ ) with low metal concentrations ( $\Sigma\text{Zn}+\text{Cu}+\text{Cd}+\text{Ni}+\text{Co}+\text{Pb}$ : 322–602  $\mu\text{g L}^{-1}$ ). No relevant difference exists between the chemical composition of the stream sediments and waters collected outside and inside the mine influence.

The partition coefficient ( $K_d$  in  $\text{kg L}^{-1}$ ) is the ratio between a pollutant concentration in sediment ( $C_s$  in  $\text{mg kg}^{-1}$ ) and its concentration in water ( $C_w$  in  $\text{mg L}^{-1}$ ) in an equilibrated water-sediment system. The partition coefficient is a useful parameter to determine the behaviour of PTE in a water sediment environment and reflects the potential eco-hazard of pollutant migration between the solid-phase and the water-phase. The log  $K_d$  of the stream sediments and water as well as their respective mean are presented in table 1.

The partition coefficient between stream sediments and water ranges between 1.60 and 5.26  $\text{kg L}^{-1}$  for the analysed PTE (table 1). The log  $K_d$  of the stream sediments/water from mine site were compared with those from USEPA (2005) and IAEA (2010). The comparison of partition coefficient with those defined will suggest if the PTE are present at the study site more likely to remain in solution (and consequently pose higher ecological risk) or to be adsorbed on solid material.

The mean log  $K_d$  for Co, Cr, Cu and Pb is lower than the mean for log  $K_d$  from USEPA (2005), which could suggest a predominant divalent forms and, consequently, to be released from sediments to the overlying water. The partition coefficient between stream sediments and water ranges from 2.42–3.18  $\text{kg L}^{-1}$  ( $K_d\text{Th}$  mean 2.74) for Th, which is lower than the mean value ( $K_d = 2.5 \text{ kg L}^{-1}$ ) indicated by IAEA (2010), suggesting that Th has more affinity to be in solution (Th water concentration: 0.015–0.044  $\text{mg L}^{-1}$ ). The  $K_d$  values for U (2.43–4.20  $\text{kg L}^{-1}$ ;  $K_d\text{U}$  mean 2.97) and for As (2.27–3.11  $\text{kg L}^{-1}$ ;  $K_d\text{As}$  mean 2.73) indicate that these elements tend to be absorbed on complex phases of stream sediments, which could be suggested by the low variability of U and As water contents with increasing distance from mine site (U: 0.070–0.084  $\text{mg L}^{-1}$ ; As 0.018–0.028  $\text{mg L}^{-1}$ ).

The increase of thorium uncharged complexes may justify the tendency of Th to be released into solution. However, locally an increase in Th concentration is observed in stream sediments from upstream to downstream, probably due to the occurrence of negative Th charge complexes with a great affinity to be adsorbed by organic matter (e.g. Mortvedt 1994; Wang et al. 2017) and Fe oxy-hydroxides (e.g. Barnett et al. 2000).

**Table 1** Partition coefficient (log  $K_d$ ) of potentially toxic elements between stream sediments and water

	Fe	Mn	Cu	Al	Zn	Ni	Pb	Co	Cr	As	Th	U
Outside mine influence												
CL3	5.22	3.59	2.40	5.20	3.16	1.86	2.70	1.84	2.30	2.60	2.96	2.60
CL5	5.43	3.85	2.45	5.38	3.05	0.99	2.08	1.50	1.64	2.83	3.18	3.17
Downstream of the open-pit lake and dumps												
CL1	5.28	3.81	1.89	5.12	3.14	4.57	2.16	1.46	1.79	3.11	2.61	2.87
CL2	5.22	3.67	2.14	5.25	3.17	1.48	2.25	1.49	1.98	2.69	2.55	2.70
CL3	5.43	3.68	2.32	5.23	3.07	2.01	2.47	1.74	2.24	2.67	3.07	2.83
CL4	5.20	3.72	2.31	5.27	3.04	1.69	2.32	1.50	1.98	2.76	2.56	2.43
CL8	4.95	3.79	2.02	4.95	3.08	1.13	1.98	1.47	1.61	2.27	2.90	4.20
CL9	5.33	3.99	2.55	5.34	3.19	1.70	2.44	1.94	2.03	3.06	2.57	3.26
CL10	5.17	3.83	2.34	5.07	3.18	1.67	2.33	1.63	2.08	2.78	2.42	3.02
CL14	5.33	3.68	2.34	5.16	3.17	1.74	2.20	1.43	2.04	2.54	2.61	2.59
Mean	5.26	3.76	2.27	5.20	3.13	1.88	2.29	1.60	1.97	2.73	2.74	2.97
*Median	–		4.2		2.7		5.1	3.3	4.5	2.5	5.28	0.7
*Range	–		0.7–6.2		1.5–6.2		2.0–7.0	2.9–3.6	–	1.6–4.3	3.1–7.4	1.3–3.0

\*USEPA (2005), IAEA (2010); not defined

The values of  $\log K_d$  for U tends to be higher than those reported by IAEA (2010), which is consistent with a local decrease in average U contents in the water samples due to the adsorption by stream sediments. Within a pH range of 5.2–7.2, U occurs mainly in hydrolysed forms (Coward and Burnett 1994; Barnett et al. 2000). Therefore, in slightly acidic and near-neutral conditions, U complexes are adsorbed on Fe mineral surfaces (e.g. Cheng et al. 2007; Zielinski et al. 2008; Gavrilesco et al. 2009; Li and Kaplan 2012; Tserenpil et al. 2013).

Most studies reported a decrease of PTE with distance from the potential contamination source (e.g. Wang et al. 2017). However, this is not observed in the studied mine site and more sampling points located far away will be required. The levels of As, U and Th contents in stream sediments are evidence of their role in the immobilization of these elements, reducing the potential contamination of mine drainage water.

## Conclusions

In this study, the water-stream sediment interaction that occurred in an abandoned uranium mine site in central Portugal was investigated. The abandoned uranium mines are located in a geochemically eminent uraniferous region in Portugal, where other uranium mines have also been abandoned. In these old mines, open-pit and mine dumps were left in the area.

The chemical composition of the stream sediments and waters collected suggest that mine influence remains far away of the mine site. The analytical data generated during this study indicate that U, Th and As in the open-pit water are similar to those of downstream water, which indicates the lake's influence on downstream aquatic systems. In downstream sediment, the partition coefficients determined in the mine site area suggest the adsorption of PTE by Fe-oxy-hydroxides. Generally, in abandoned U mines, PTE concentrations tend to decrease downstream. This small mine site presently does not appear to represent a substantial environmental concern at the present data according to the obtained results.

The results suggest that stream sediments are a water quality indicator and contribute to water management and ecological risk in abandoned mine areas. Therefore, further studies should be carried out focusing on water-sediments interaction and mineral speciation modelling, including mineralogical characterization, to identify functional processes that regulate water quality.

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