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Mobility of Uranium in Groundwater-Surface Water Systems in a Post-Mining Context (Central Portugal)

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Abstract

In uranium abandoned mine areas, particularly with mine tailings and open-pit lakes, the mobility of potentially toxic elements still acts as a source of surface and groundwater contamination. The water of open-pit lakes from Ribeira de Bôco mine and associated groundwater and surface water from the area is neutral and with low metal contents. However, some water samples are contaminated with Cd, Cr, Cu, Fe, Mn, As, and U and should not be used for human consumption or in agricultural activities. The baseline uranium threshold is considerably high for groundwater, which is supported by geogenic features and mining activities.

Keywords: Geogenic Contents, Uranium mines, Surface and Groundwater, Contamination

Introduction

Water resources has become a serious environmental problem on a global scale. Nowadays, the global concern is to ensure sufficiency in water quantity for public health, food security, and water access demand (UNESCO, 2019). However, this natural resource is becoming scarce because of increased consumption, extended droughts, and water quality degradation, mainly associated to anthropogenic activities (Satapathy *et al.*, 2009; Val *et al.*, 2019; Mello *et al.*, 2020). Future scenarios for water resources are predicting water scarcity, with a decrease in the amount of precipitation and limitation on groundwater recharge for the next five decades.

The impact from mine waste on socio-economically disadvantaged communities worldwide continues to be documented on surface-groundwater systems (e.g., Dambacher *et al.*, 2007; Jiang *et al.*, 2015; Babayan *et al.*, 2019; Pal and Mandal, 2019; Flett *et al.*, 2021). Pollution studies associated with uranium mines are commonly carried out within the context of watersheds (e.g., Fernandes and Franklin, 2001; Winde, 2010).

In Portugal, for 80 years ago, uranium mining activities ceased leaving as a legacy over 61 radioactive ore deposits involving uranium and radium production. These mining activities have been abandoned into the environment, without recovery processes, and the resulted areas contain tailings and rejected materials deposited and exposed to the air and water since those years. Consequently, uranium and potentially toxic elements (PTE) are leaching on these areas, which act as a source of surface and groundwater contamination (e.g., Antunes *et al.*, 2020; Neiva *et al.*, 2019).

Uranium and arsenic contamination pose a concern for the protection of the environment and for water quality (Skierszkan *et al.* 2020). Geochemical environment, groundwater provenance and hydrogeochemistry will affect the mobility of selected metals and As (e.g., Bird *et al.* 2020), particularly in post-mining contexts. Growing worldwide concern over uranium contamination of groundwater resources has placed an emphasis on understanding uranium mobility and potential toxicity in groundwater-surface water systems (Byrne *et al.*, 2021).

The purpose of this study is to identify the geochemical characteristics of surface and groundwater with a particular focus on uranium and other trace elements mobility in an abandoned uranium mine from Portugal, where water resources are scarce and consequently a regularly monitoring and quality is needed for integrated water management.

Study area

In Portugal, between 1908 and 2001, different deposits of radioactive ore were extracted from the production of radium and uranium (north and central Portugal). The old uranium mine of Ribeira do Bôco (40˚31´17´´N; 7˚38´26´´W) is located about 2.5 km SW from Arcozelo village (Gouveia, central Portugal). The area is in the Central Iberian Zone of the Iberian Massif (e.g., Farias *et al*., 1987), which is one of the many mines from the uranium-bearing Beiras area. The ore deposit is mainly of supergenic nature with dominant mineralization in autunite and torbernite. The regional geology is characterized by smoky and zoned quartz veins and basic rocks with pitchblende, sulphides, and secondary uranium minerals (Cameron, 1982). Underground exploitation resulted in waste rock dumps with high concentration of radionuclides. High levels of radiation have been reported in the surrounding water and soil (Carvalho, 2014).

The mine was exploited in two open-pit mines, located on the east of the Ribeira de Bôco stream, between 1986 and 1988. A total of 32.5 tons of ore were exploited with an average content of 0.97% U_3O_8 and containing 31.7 kg of U_3O_8. The pit lake contains approximately 108,000 m^3 of water, with 20 meters deeper (Fig. 1a). Two dumps containing tailings, waste rocks, and rejected material from the mine exploration (total of 39,580 m^3) are located close to the open pit lake and are slightly covered by vegetation but was not yet restored (Fig. 1b). Surface runoff and mine water are discharged into a small creek, which displays typical features of mine contamination, such as deposition of yellow-reddish precipitates (Fig. 1c, d).

The area has rural characteristics with vegetation that is dense and mainly with herbaceous species (Fig. 1e). Around the abandoned mine, small agricultural areas occur with potato crops, vineyards, and pastures (Fig. 1f), which are irrigated by the Ribeira de Bôco stream and wells located in the stream margins.

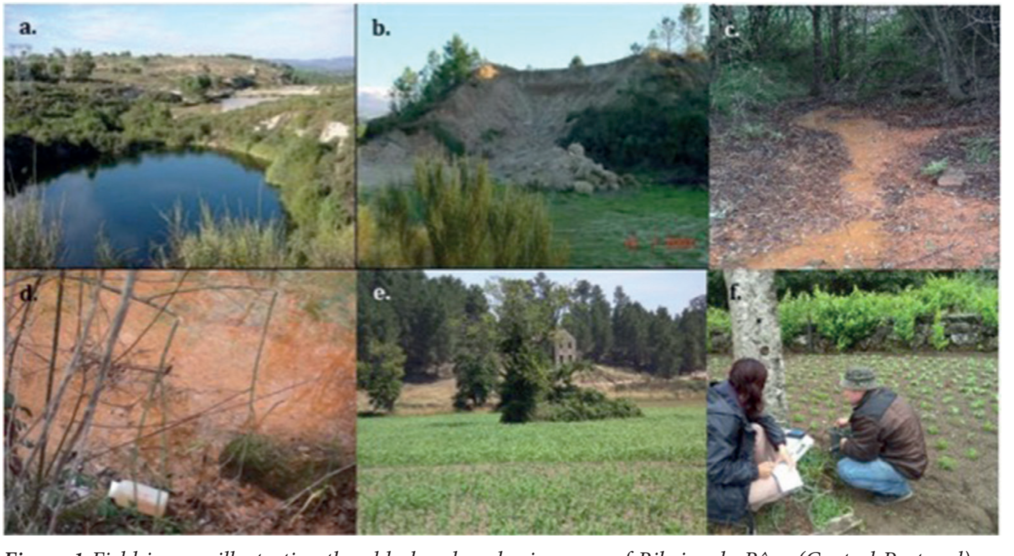

Figure 1 *Field images illustrating the old abandoned mine area of Ribeira do Bôco (Central Portugal): a. open pit lake; b. mine dumps; c, d. water mine with ochre-precipitates; e. vegetation and crops; f. well in an agricultural area.*

Methods

A total of twenty-one water samples, corresponding to open pit water (Rb2, 6, 16, 24), water mine drainage (Rb5), surface water (Rb1, 3, 7, 9, 11, 13, 15, 19, 22), and groundwater (Rb4, 8, 10, 12, 14, 17, 18, 23), were selected on the study area (Fig. 2). The temporal variability of water was represented by two sampling campaigns, during a hydrological year, and representing the raining and dried seasons. All water samples were collected, and analysed for physico-chemical properties, as well as selected potentially toxic elements. The water points located outside mine influence area (Rb18, 19, 22, 23; Fig. 2) have been selected to characterize the natural geochemistry of the area. The distribution of water sampling points was not uniform due to the nonuniformity of well distribution and water stream availability. The main purpose of the wells is for water supply to residents, and domestic animals and agricultural irrigation.

Temperature, pH, Eh, and electrical conductivity (EC) were measured in situ using a multiparameter HANNA HI929828 model. The water samples were filtered through 0.45 µm pore size membrane filters. Those for the determinations of major and trace elements (e.g., Ca, Mg, Fe, U, Th, As, Co, Cd, Pb, Cu, Zn, and Mn) were acidified with suprapur HNO3 at pH 2 and analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES), using a Horiba Jovin Yvon JV2000 2 spectrometer. Anions were determined in non-acidified samples by ion chromatography with a Dionex ICS 3000 Model. Duplicate blanks and laboratory water standards were analysed to assess quality control of the obtained results. The accuracy of the methods was verified using certified patterns and the measurement precision was greater than 5%. The laboratory water analyses were obtained at the Department of Earth Sciences, University of Coimbra, Portugal.

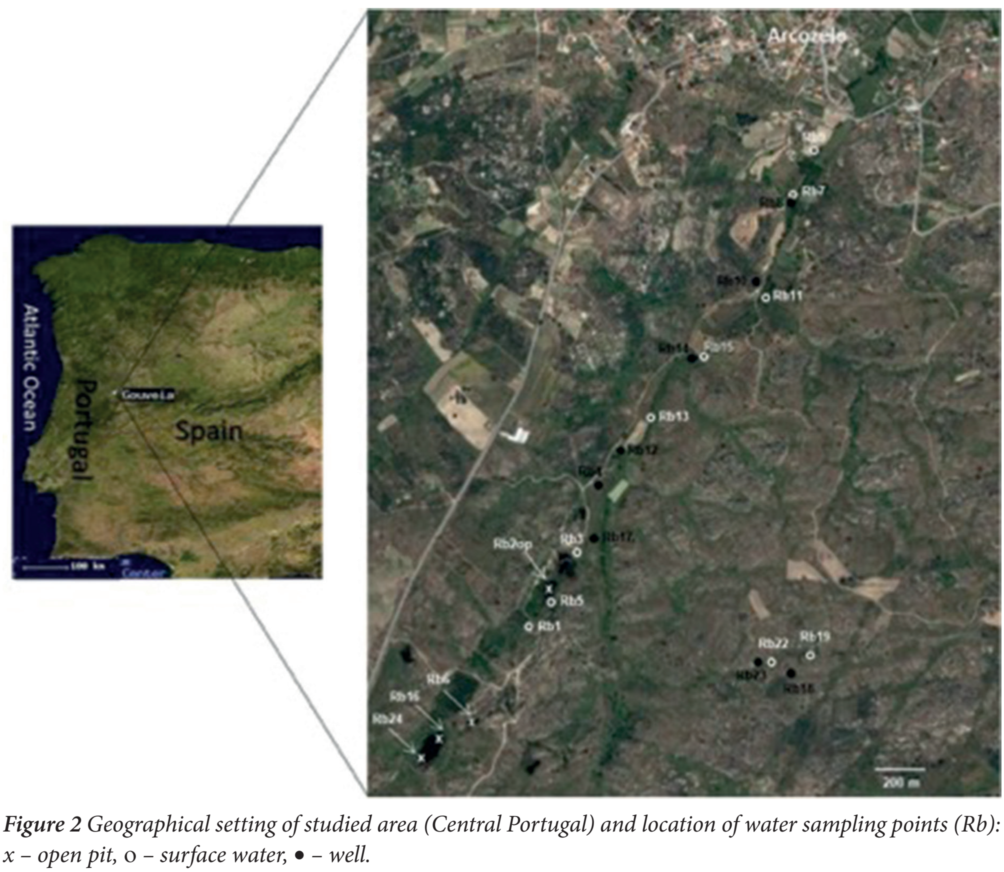

Figure 2 Geographical setting of studied area (Central Portugal) and location of water sampling points (Rb): x – open pit, o – surface water, • – well.

Results

The Piper diagram shows the main geochemical characteristics of the water from Ribeira de Bôco area, considering the water samples collected upstream and downstream mine influence (Fig. 3a, b). The dominant hydrochemical facies of most water samples is undefined type or locally $(Na+K)-SO_4^{2-}$ while the water collected on the influence of mine area, shows a $(Na+K)-Cl^-$ water type to undefined one, according to Piper's classification. There is no significant variation between the water collected on the raining and dried period (Fig. 3).

The hydrochemical processes that control chemistry in the study area could be expressed by the contribution of major ions to the water mineralization (expressed through the EC). However, the water has lower mineralization and the correlation found between EC and major ions are lower ($R2$: EC-SO_4^{2-} = 0.2182; EC-Mg = 0.0311; EC-Cl- = 0.0732; Na-Cl = 0.0732), otherwise the bicarbonate ion appears with a better correlation ($R2$: EC-HCO3 = 0.7001; EC-Ca = 0.8893; EC-Na = 0.7652), suggesting the influence of water-rock interaction processes, including weathering of minerals, with release of alkaline metals and production of alkalinity. Particularly on surface water, these correlations seem to corroborate higher geological and agricultural activity contributions.

Most water samples are neutral (pH ranges from 5.5 to 7.4) and showing low metal content (EC = 22-264 µS/cm; TDS = 4-157 mg/L). The spatial geochemical variability indicates that the water collected under the influence of mine activities tend to present the highest EC and TDS values, and HCO3-, K, Ca, Mg, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sr, and As contents. However, there is no significant variation on water composition between raining and dry period.

The water sample Rb5, receiving water mine drainage, is the most mineralized water and contains the highest contents of Fe, Mn, Cd, Sr and As (Table 1). The highest Fe (up to 20.1 mg/L) and Mn (2.9 mg/L) contents are supported by the occurrence of yellow-reddish precipitates (Fig. 1c, d).

The maximum contents of As, Th and U in groundwater are higher than water from the open pit (Table 1), probably due to pH-Eh conditions. In the area, there is an elevated U and As baseline in groundwater and surface water. Regional uranium mobilization is sufficient to produce water U-enrichment, which is promoted by the weathering of sulphide-ore deposits and consequent U concentration into fractures around ore deposits that might act as preferential conduits for groundwater flow and chemical weathering.

Some water samples are contaminated with Cd, Cr, Cu, Fe, Mn, As and U and

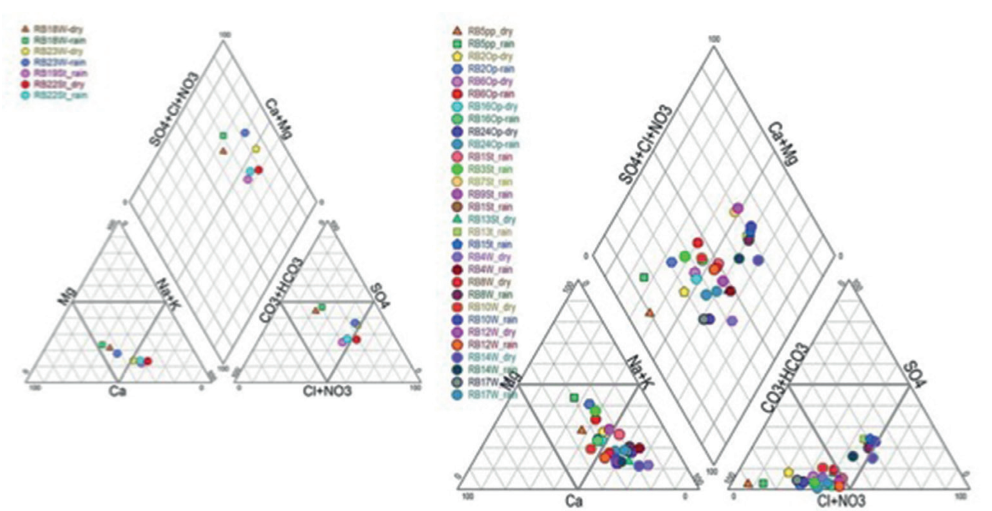

Figure 3 Hydrochemistry classification (Piper diagram) of the water from the Ribeira de Bôco area: a. water samples located outside mine influence; b. water samples in the mine influence.

Table 1 Minimum and maximum values obtained in the water from Ribeira do Bôco area.

	EC	Fe	Mn	Cd	Co	Cr	Cu	Ni	Pb	Sr	Zn	As	Th	U
	(µS/cm)	mg/L		µg/L										
Open pit	35-103	0.01-0.22	0.01-0.08	2.7-26.0	nd - 11.8	14.9-47.3	nd - 13.1	nd - 13.0	3.3-14.8	15.3-27.0	nd - 23.3	28.5-48.6	11.2-31.5	nd - 60.0
Rb5 (mine drainage)	248-264	15.4-20.1	1.5-2.9	44.3-79.6	4.7-11.4	21.8-37.5	nd - 10.5	nd - 10.5	6.8-17.4	79.2-80.2	nd - 22.8	74.7-76.6	30.7-23.9	31.2-54.2
Surface water	23-103	nd -0.21	0.01-0.08	6.6-28.8	nd - 11.8	22.2-54.0	nd - 13.5	nd - 16.2	9.5-16.6	13.3-40.9	nd - 178.0	29.2-54.4	14.1-31.7	23.3-89.2
Groundwater	22-162	nd - 1.16	0.01-0.22	6.3-37.2	nd - 12.2	21.9-51.9	nd - 12.3	nd - 13.5	5.7-18.3	5.9-52.8	nd - 41.6	24.9-54.5	11.1-32.4	nd - 83.3

should not be used for human consumption or in agricultural activities, considering water framework referenced values (Portuguese Decree, 1998; 2017; World Human Organization, 2011).

Conclusions

Mining regions constitute an important challenge in the management of water resources since its impacts could be an environmental risk and human health concern.

Portugal has important resources of groundwater that may be strategic to face the expected dry years to come. Furthermore, regularly monitoring and evaluating groundwater quality is needed for integrated management and policy making.

In the surveyed area, the baseline threshold of some potentially toxic elements is considerably high, in which concerns to groundwater and surface water. The natural geogenic conditions (geological setting and local geology) and mining activities are the main control on the mobility of potentially toxic elements in the groundwater-surface water systems, particularly in this post-mining affected area.

Development of methods to establish the location of contaminated groundwater entry to surface water environments, and the potential effects on ecosystems, is crucial to develop both site-specific and general conceptual models of uranium behaviour and potential toxicity in affected surface and groundwater environments, which will be a support to the application of adequate preventive and monitoring methodologies in post-mining contexts.

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