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Spatial surface and groundwater interaction in an abandoned radium-bearing mine (Guarda, central Portugal)

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Abstract

The abandoned Alto da Várzea radium mine exploited quartz veins containing ore minerals and U-bearing minerals, such as autunite and torbernite. The area is located on a Variscan two-mica granite that intruded the schist–greywacke complex. The mine was exploited underground from 1911-22 and was closed down in 1946. This mine was not restored and actually a commercial area is deployed. A total of ten surface water and groundwater samples were collected in the study area between 2008/09. Most water samples have pH values ranging from 4.3 to 6.8 and are poorly mineralized (EC=41-186 µS/cm; TDS=33-172 mg/L). However, the waters are contaminated with NO_2^-, Mn, Cu, As and U and must not be used for human consumption and some of them in agricultural activities. The water contamination is mainly associated with the old radium mine and human activities developed in the area.

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Keywords: radium mine; water; contamination; remediation; central Portugal

1. Introduction

In Portugal, between 1908 and 2001, about 60 deposits of radioactive ore were extracted from the production of radium and uranium[1]. Following closure, the Portuguese mines were abandoned and local areas of former radium and uranium mines were studied for environmental radioactivity, stable metals and public health impact[1-4].

Mining can be regarded as a potentially harmful activity to surface water and groundwater. The extraction of radioactive ore produces tailings, large volumes of contaminated waste rocks and heap-leach residues accumulated in the dumps at mine sites. The discharges of uranium and associated heavy metals and metalloids from waste and

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tailing dumps in abandoned uranium mining and processing sites pose contamination risks to surface water and groundwater[5,6]. The present sulfides are oxidized, causing acidification of water and the discharge of metals to the environment. In wet climates, acid mine drainage development and leaching of dumps are dominant pathways of contaminants into the surrounding environment.

The purpose of this study is to characterize the spatial and temporal variability of some chemical properties and trace element contents in surface water and groundwater associated with the old mine of Alto da Várzea, 65 years after closure. The obtained results will allow to assess the impacts of the abandoned mine and can improve remediation processes in the study area and avoid similar problems in other mine areas.

2. The mine site

The Alto da Varzea mine (AV mine) site is located at the southeastern of the town of Guarda, in Central Portugal (Fig. 1a). Geologically, the study area belongs to the Central Iberian Zone of the Iberian Massif. This area consists of a Variscan porphyritic two-mica granite which intruded the schist-greywacke complex[7].

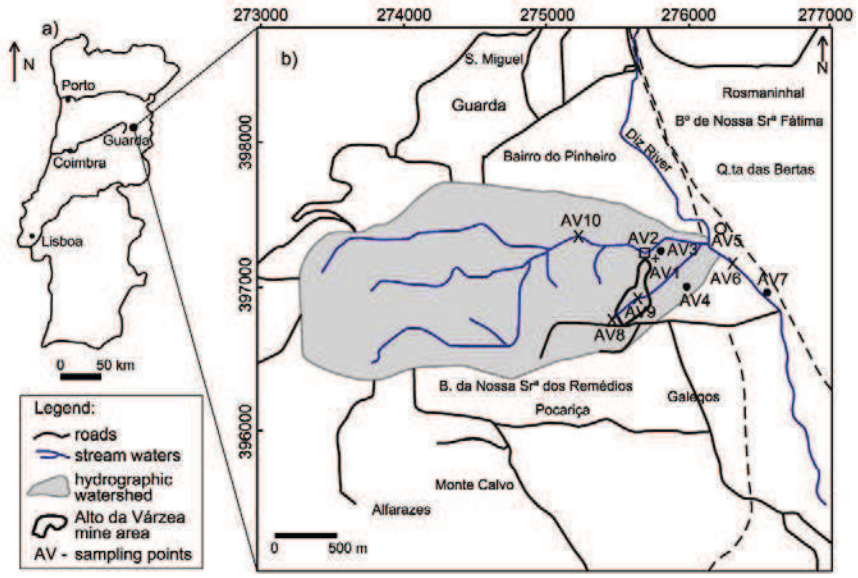

Fig. 1. a) Location of the study area (Alto da Várzea - Guarda) on the map of Portugal; b) water sample collection sites included in the stream watershed. Waters collected in: a mine dump (+ AV1); mine gallery (□ AV2); well (● AV3, AV4 and AV7); spring (○ AV5) and stream water (x AV6, AV8, AV9 and AV10).

The mine consists of a mineralized quartz vein trending N25-30º E/SW, up to 5 m thick at depth associated with altered granite and jasper veins. It contains secondary U-minerals which are autunite ($Ca(UO_2)_2(PO_4)_2.10\text{-}12H_2O$) and torbernite ($Cu(UO_2)_2(PO_4)_2.11H_2O$)[7].

The mine was exploited underground and had three levels and a gallery at the hillside. The mine exploited radium retained in ore minerals from 1911-22 and was closed down in 1946. The mine is located in a soft slope area with altitudes ranging from 810 to 840 m. The surface drainage runs to SE towards the Diz stream, which has a very low water flux in summer. One dump retained the waste from the mine exploration and contained about 2000 ton of leached materials without any compact[7]. This mine area was not restored and actually a commercial area is deployed. The area is covered by vegetation, consisting mostly of oaks, pasture and agricultural zones.

3. Water sampling and analyses

A total of ten sampling points was chosen to collect water samples four times, in summer (July 2008 and 2009), winter (January 2009) and spring (April 2009), obtaining a total of 35 water samples. One sampling point received drainage water from: a mine dump (sample AV1), a mine gallery (sample AV2) and a spring (AV5), three water samples were obtained in wells (samples AV3, AV4 and AV7) and streams (samples AV6, AV8 and AV9). These nine water samples are considered in the mine influence area (the area affected by the mine exploitation). One water sample was collected upstream the mine area and is considered outside the mine influence area (sample AV10) (Fig. 1b). Waters were collected about 20 cm below the surface of the water level. Temperature, pH, Eh, dissolved oxygen (DO), electrical conductivity (EC) and alkalinity were measured in situ. The samples were filtered through 0.45 µm pore size membrane filters. The determinations were carried out in the Department of Earth Sciences, University of Coimbra (Portugal). Cations were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; Horiba Jovin Yvon JV2000 2 spectrometer with a monochromator), in HNO_3 acidified samples (pH = 2), while anions were determined in non-acidified samples by ion chromatography (Dionex ICS 3000 Model). The detection limits in µg L^{-1} were 0.01 for K, Ca and Th; 0.02 for Na, Al, Pb, Ni, As and U; 0.22 for Sr; 0.38 for Li; 1.43 for Mn; 1.47 for B; 1.54 for Co; 1.92 for Zn; 2.1 for Cr; 2.2 for Cu and Cd; 2.8 for Ba; 3.2 for Fe; 5.76 for Mg; 0.93 for F^-; 1.32 for Cl^-; 1.20 for NO_2^-; 1.37 for NO_3^-; 2.27 for SO_4^{2-} and 1.19 for PO_4^{3-}. The accuracy and precision for water analysis were obtained by inserting two subsamples of an external standard (Relacre, report EAA.2007Fev.V0) within each batch of ten water samples. The calculations were carried according to defined methodologies[8,9] and the obtained results were accepted (Table 1). Total dissolved solids (TDS) resulted in the weight of material by evaporating 100 ml of filtered water. Ion balance errors of the analytical data were within $\pm$ 15%.

Table 1. Allowance of accuracy and precision for routine analyses of waters from Alto da Várzea.

	Accuracy	Precision
Concentration range	$\overline{\Delta lgC} = \lvert lg\overline{C_i} - lgC_s \rvert$	$\lambda = \sqrt{\frac{\sum_{i=1}^{n}(lgC_i - lgC_s)^2}{n-1}}$
< 3 detection limit	≤ 0.29	0.43
> 3 detection limit	≤ 0.12	0.16

$\overline{C_i}$- the average determined value of the standard Relacre$_i$; C_i - the determined value of the standard relacre; C_s - the recommended value of the standard Relacre for water.

4. Results and Conclusions

The abandoned mine area is located close to a rural area and some of its water is used for agricultural irrigation. The pH values ranged from 4.3 to 6.8 with more acidic values during summer than winter. Most waters are poorly mineralized (EC=41-186 µS cm^{-1}), which was also supported by the total dissolved solids (TDS), ranging from 33 to 172 mg L^{-1}. The highest EC, TDS and PO_4^{3-} values occur in a stream water (water sample AV6: EC=636 µS cm^{-1}, TDS=352 mg L^{-1} and PO_4^{3-}=53 mg L^{-1}) and in a well (water sample AV7: EC=396 µS cm^{-1} and TDS=237 mg L^{-1}), which received drainage from domestic and agricultural activities. There are no significant differences between water sample collected outside the mine influence (water sample AV10) and the water samples located inside the mine influence area (Fig. 2). Most of water samples have low metal concentrations and are classified as neutral-metal poor to acid-metal poor when plotted in the Ficklin diagram. According to the Piper classification, the hydrochemical facies of most water samples is undefined type or Na-HCO_3- type. The water from the mine gallery tends to present the highest contents of F^- (up to 0.31 mg L^{-1}), Mn (up to 1450 µg L^{-1}), Li (up to 58 µg L^{-1}) and U (up to 66 µg L^{-1}) (Fig. 2). In general, there are higher U water contents in April and July 2009 and lower U contents during January 2009, probably due to a dilution effect. Most waters are contaminated in NO_2^- (3.5 mg L^{-1}), Mn, Cu (77 mg L^{-1}), As (33 mg L^{-1}) and U and must not be used for human consumption (Fig. 2). Some water points (water samples: AV2, AV7 and AV9) are also contaminated in Mn and could not be used in agricultural activities (Fig. 2). The water contamination is mainly associated with the old radium mine and human activities. The isotopic Ra^{226}

content of waters associated with the AV mine range between 0.050 and 0.145 Bq L^{-1} and are below the legislation defined value[7].

The obtained results in surface water and groundwater associated with the Alto da Várzea abandoned radium mine, reinforces the evidence of environmental and human health risks associated with old abandoned mining areas and the definition and application of adequate remediation methodologies.

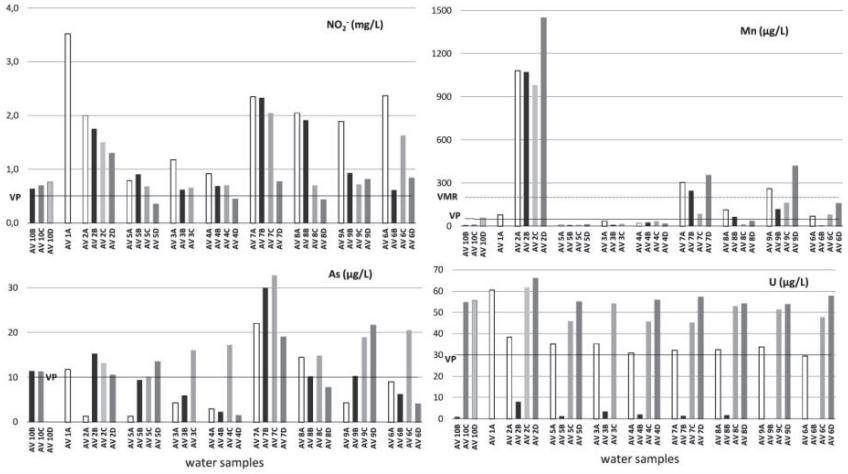

Fig. 2. Seasonal chemical variations in waters from the abandoned Alto da Várzea mine area.
Water samples: mine dump (AV1), mine gallery (AV2), spring (AV5), well (AV3, AV4 and AV7) and streams (AV10, AV8, AV9 and AV6). Waters collected during: A) July 2008; B) January 2009; C) April 2009; D) July 2009. VP – permitted value for human consumption; VMR – recommended value for human consumption[10,11], except for U[12].

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