Spatial water interaction in radium/uranium mines – a Portuguese case study

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Abstract

The extraction of radioactive ore produces tailings and large volumes of waste rocks accumulated in the dumps. The abandoned Picoto radium mine area is located close to Vilar Seco village (Portugal). The mineralization occurs in quartz veins, with torbernite, meta-torbernite and uranophane, and some U-bearing minerals. The mine is in a soft slope area, with altitudes ranging from 360-380 m, included in the Cagavaio river catchment.

The mining works were developed in surface and underground. First radium exploitation was carried out between 1917-21, in two open pit mines. Later, from 1950-53, the exploitation was reactivated, in underground galleries, to produce uranium. This mine was closed in 1953 and never has been restored. A local growing area was developed, mainly for vineyards and agricultural products. Three dumps contain about 35000 tonnes of wastes and is slightly covered by vegetation.

A total of ten surface water and groundwater samples were collected. Most waters have pH values from 4.7 to 6.3 and are poorly mineralized (EC=45-224 µS/cm; TDS=17-150 mg/L). However, some waters are contaminated with NO_{2^-}, Fe, Mn, As and U. The drainage waters must be controlled within a temporal and spatial monitoring.

Keywords: radium/uranium mines, water, contamination, remediation, central Portugal

Introduction

Mine activities have a potentially harmful effect in 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. Associated sulphur bearing minerals are oxidised, causing acidification of water and the release of metals. The erosion and weathering of dumps cause contamination of surface water and groundwater (e.g. Gómez et al. 2006; Antunes et al. 2018) leading to contamination of stream sediments and soils (e.g. Lottermoser et al. 2005; Lottermoser and Ashley 2006; Kipp et al. 2009). Particularly, in the wet season and wet climates, acid mine drainage development and leaching of dumps are dominant pathways of contaminants into the surrounding environment.

Uranium mining within Europe reached its height between 1960 and 1990, after which the deposits became depleted and mines closed (Dittmar 2013). Consequently, there are about 150 uranium mines in the EU (Raeva et al. 2014; Falck 2015). In Portugal, about 60 radioactive ore deposits were exploited, between 1908 and 2001, to produce radium and uranium (Carvalho 2014). These mines were abandoned, and local areas were studied to assess the influence of environmental radioactivity and potentially toxic elements in the public health (e.g., Pinto et al. 2004; Carvalho et al. 2013; Carvalho 2014, Neiva et al. 2014, 2015, 2016; Antunes et al. 2016, 2018).

The main purpose of this study is to characterize the spatial water interaction in a radium/uranium mine area and temporal variability of some chemical proprieties and trace element contents in surface water and groundwater associated with the old Picoto mine, 65 years after the closure.

Methods

The abandoned Picoto mine area is located at the Central Iberian Zone of the Iberian Massif (ZCI), close to Vilar Seco village, southeast of Viseu, central Portugal. The area is included in the catchment of the Cagavaio river, with dominant drainage NE-SW, and in a soft slope topography, with altitudes ranging between 360 and 380 m (Fig. 1).

In this area, a Variscan porphyritic biotite>muscovite granite (late- to post-D3) occurs and intruded the Beiras Group complex (previously called Schist-greywacke Complex), containing phyllites and metagreywackes (Oliveira et al. 1992; Azevedo et al. 2005). The medium- to coarse -grained porphyritic granite, with biotite>muscovite, contains up to 9-17 mg/L U, in uranium bearing minerals, such as uraninite, zircon and monazite (Cotelo Neiva 2003). Granite is affected by different episiensitization degrees (Teixeira et al. 2010).

The mineralization occurs mainly in quartz veins intruding the granite. These quartz veins fill faults and fractures trending N37°-45° E and N50°-70° E, locally brecciated (Cotelo Neiva 2003). The meta-torbernite and uranophane, together with some U-bearing minerals such as chlorite and Fe-Mn-hydroxides, and pyrite, occur in the quartz and disseminated microfractures (Teixeira et al. 2010).

The mining activity took place in open pits and underground. Between 1917 and 1921, an inicial radium exploitation was developed in two open-pit mines (NE Rio Cagavaio). After that, between 1950/53, uranium was exploited in underground galleries, about 150 m long. The mine ceased its activity in 1953, leaving three waste heaps, with about 35 000 tonnes, without any intervention and rehabilitation measures. Nowadays, the area is occupied by local crops, especially vineyard and agricultural products mainly to local human consumption.

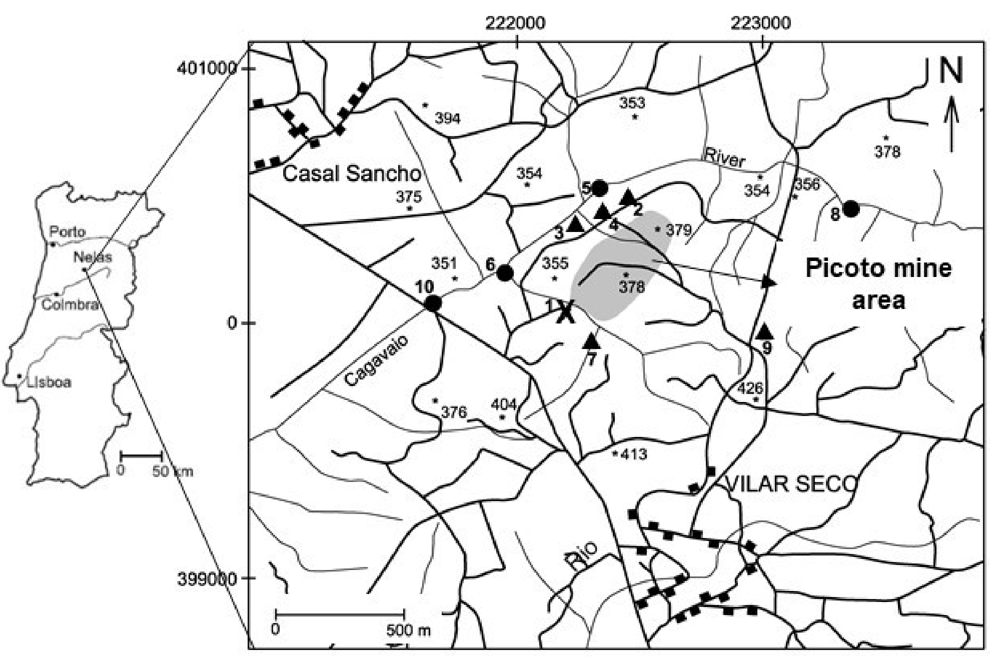

Figure 1 Geographic setting of the Picoto mine area and location of water sampling points (Surface water: ● – stream water; groundwater: X - spring; ▲- well).

A total of ten sampling points was chosen to collect surface water (samples: 5, 6, 8 and 10) and groundwater (samples: 1, 2, 3, 4, 7 and 9), twice in a hydrological year, representative of the dry (summer) and raining period (winter). The water samples 8 and 9 were collected upstream the mine area, located outside the mine influence, and representing the local background (Fig. 1). Waters were collected about 20 cm below the surface of the water level. Temperature, pH, Eh, dissolved oxygen (DO), Total Dissolved Solids (TDS), Electrical Conductivity (EC) and alkalinity were determined "in situ". The samples were filtered through 0.45 µm pore size membrane filters. Those for the determinations of cations were acidified with HNO_3 at pH 2 and analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using a Horiba Jovin Yvon JV2000 2 spectrometer with a monochromator. Anions were determined in non-acidified samples by ion chromatography with a Dionex ICS 3000 Model. Duplicate blanks and a laboratory water standard were analysed for quality control. The validation of the precision of the analytical results was performed according to the methodologies of Xuejing (1995) and Min et al. (2014). The determinations were carried out in the Department of Earth Sciences, University of Coimbra, Portugal.

Results

The abandoned mine area of Picoto is located close to a rural area, in the vicinity of Vilar Seco, and some of its water is used for agricultural irrigation.

In general, the waters are acidic or near neutral, with pH values ranging from 4.7 to 6.3, with the most acid value obtained in the surface water receiving drainage from the Picoto mine area (water sample 6; Fig. 1). Most waters are poorly mineralized (EC=45-224 µS/cm), which is supported by the values of total dissolved solids (TDS), ranging from 17 to 150 mg/L. According to the Piper classification, the dominant hydrochemical water facies is of undefined type or Na-Cl-HCO_3^- water type.

The water samples have high metal contents and are classified as acid to near-neutral in the Ficklin diagram (Fig. 2). There

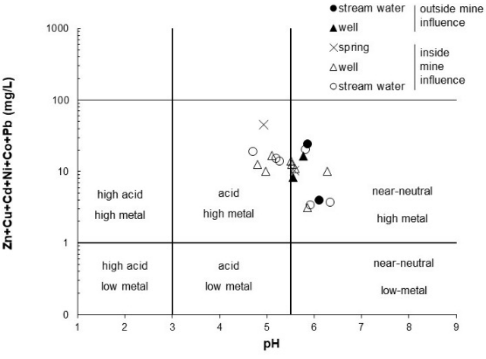

Figure 2 Classification of the waters from the Picoto mine area in the Ficklin diagram (Ficklin et al. 1992).

is no significant difference between the chemical composition of the waters collected outside the mine influence (water points 8 and 9, Fig. 1) and the waters located inside the mine influence (Fig. 2).

During the dry period, the waters tend to be more acidic and have higher EC values, particularly groundwater (springs and wells). Sulphide oxidation of the mineralized veins, now accumulated in the tailings and heaps, produce the most acid water, and increase the leaching and solubility of potentially toxic elements (e.g. Antunes et al. 2016, 2018).

In general, in the dry period, there are higher NO_2, Fe, Cu and As water contents than in the rainy period, probably due to a concentration effect (Fig. 3). Most of the waters does not present significant variation in U contents between the dry and rainy period. Otherwise, Th contents tend to have higher values in the rainy season (Fig. 3), probably due to dissolution in favourable pH-Eh conditions.

However, most waters are contaminated with NO_2, Fe, Mn, Cu, As and U and should not be used for human consumption or agricultural activities (Fig. 3). The Fe and Cu water contamination occurs preferentially in the dry period, associated with lower pH values, which promotes an increase of chemical species dissolution, with the release of the metals. The water contamination is mainly associated with the old radium mine and human activities.

The results of external gamma radiation show high values, particularly near waste

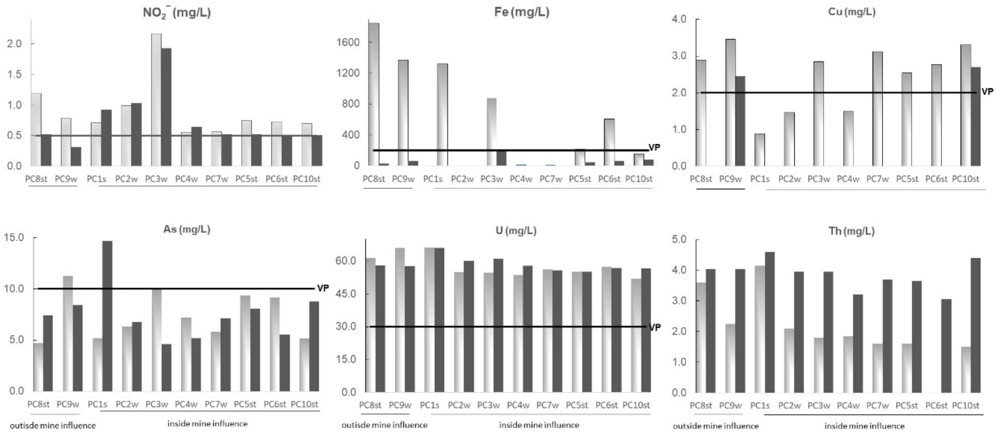

Figure 3 Seasonal chemical variation in waters from the Picoto mine area. Dry period (summer) - light gray; rainy period (winter) - black. Water points: st – stream water; w - well; s - spring. VP - parametric value (Portuguese Decree 1998, 2007, WHO 2011).

dumps from the mine exploitation (0.61 µGy.h-1), surpassing the regional background value for the Oliveira do Hospital region; being an indicator of radiological contamination due to mining activity (EDM 2007).

Conclusions

In the studied area, water contamination is mainly associated with old mine activities for radium/uranium exploitation.

The drainage waters must be controlled with spatial and temporal monitoring.

The obtained results in surface and groundwater associated with the Picoto abandoned radium/uranium mine reinforce the evidence of environmental and human health risks associated with old abandoned mine areas and the definition and application of adequate remediation and/or rehabilitation methodologies.

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References

Antunes IMHR, Neiva AMR, Albuquerque MTD, Carvalho PCS, Santos ACT, Cunha PP (2018) Potential toxic elements in stream sediments, soils and waters in an abandoned radium mine (central Portugal). Environ Geochem Health 40(1):521-542, doi:10.1007/s10653-017-9945-2

Antunes IMHR, Gomes MEP, Neiva AMR, Carvalho PCS, Santos ACT (2016) Potential risk assessment in stream sediments, soils and waters after remediation in an abandoned W>Sn mine (NE Portugal). Ecot Environ Saf 133:135-145, doi:10.1016/j.ecoenv.2016.06.045

Azevedo MR, Valle Aguado B, Nolan J, Martins M, Medina J (2005) Origin and emplacement of syn-orogenic Variscan granitoids in Iberia the Beiras massif. J Virtual Explorer, E Edition 19(7):1–18

Carvalho FP (2014) The National radioactivity monitoring program for the regions of uranium legacy sites in Portugal. Proc Earth Planet Sci 8:33-37, doi:10.1016/j.proeps.2014.05.008

Carvalho PCS, Neiva AMR, Silva MMVG, Antunes IMHR (2013) Metal and metalloid leaching from tailings into stream water and sediments in the old Ag-Pb-Zn Terramonte mine, northern Portugal. Environ Earth Sci 71/5:2029-2041, doi:10.1007/s12665-013-2605-7

Cotelo Neiva JM (2003) Jazigos portugueses de minérios de urânio e sua génese. In Ferreira (Ed.), Engineering Geology and Geological Resources, Book in honour to Prof. J.M. Cotelo

Neiva. Univ Pr. 1, p 15–76

Dittmar M (2013) The end of cheap uranium. Sci Total Environ 461–462:792–798, doi:10.1016/j.scitotenv.2013.04.035

EDM (2007) Mina do Picoto – Relatório Interno, 22 pp

Falck WE (2015) Radioactive and other environmental contamination from uranium mining and milling. Woodhead Publishing Series in Energy, 3-34, doi:10.1016/B978-1-78242-231-0.00001-6

Ficklin WH, Plumlee GS, Smith KS, McHugh JB (1992) Geochemical classification of mine drainage and natural drainage in mineralized areas. In Kharaka YK, Maet AS (Eds.), Water-rock interaction 7:81-384

Gómez P, Garralón A, Buil B, Turrero MJ, Sánchez L, De la Cruz B (2006) Modeling of geochemical processes related to uranium mobilization in the groundwater of a uranium mine. Sci Total Environ 366:295-309

Kipp GG, Stone JJ, Stetler LD (2009) Arsenic and uranium transport in sediments near abandoned uranium mines in Harding County, South Dakota. Appl Geochem 24(12):2246-2255, doi: 10.1016/j.apgeochem.2009.09.017

Lottermoser BG, Ashley PM (2006) Physical dispersion of radioactive mine waste at the rehabilitated Radium Hill uranium mine site, South Australia. Aust J Earth Sci 53: 485:499, doi: 10.1080/08120090600632383

Lottermoser BG, Ashley PM, Costelloe MT (2005) Contaminant dispersion at the rehabilitated Mary Kathleen uranium mine, Australia. Environ Geol 48: 748-761, doi: 10.1080/08120090600632383

Min L, Xiaohuan X, Guiyi X, Hangxin C, Zhongfang Y, Guohua Z, Jiayu Y, Zhonghui L (2014) National multi-purpose regional geochemical survey in China. J Geoch Explor 139:21-30, doi: 10.1016/j.gexplo.2013.06.003

Neiva AMR, Antunes IMHR, Carvalho PCS, Santos ACT (2016) Uranium and arsenic contamination in the former Mondego Sul uranium mine area, Portugal. J Geoch Explor 162:1-15, doi:10.1016/j.gexplo.2015.12.004

Neiva AMR, Carvalho PCS, Antunes IMHR, Santos ACT, Cabral-Pinto MMS (2015) Spatial and temporal variability of surface water and groundwater before and after remediation of a Portuguese uranium mine area. Chem Erde Geoch 75/3:345-356, doi:10.1016/j.chemer.2015.06.001

Neiva AMR, Carvalho PCS, Antunes IMHR, Silva MMVG, Santos ACT, Cabral-Pinto MMS (2014) Contaminated water, stream sediments and soils close to the abandoned Pinhal do Souto uranium mine, Central Portugal. J Geoch Explor 136:102-117, doi:10.1016/j.gexplo.2013.10.014

Oliveira JT, Pereira E, Ramalho M, Antunes MT, Monteiro JH (Coords.) (1992) Geological map of Portugal, 1/500 000 (5th Ed.), SGP, Lisboa

Pinto MMSC, Silva MMVG, Neiva AMR (2004) Pollution of water and stream sediments associated with the Vale de Abrutiga uranium mine, Central Portugal. Mine Water Environ 23:66-75

Portuguese Decree (1998) Decreto-Lei 236/98 – Legislação Portuguesa de Qualidade da Água. Diário da República I-A: 3676-3722

Portuguese Decree (2007) Legislação Portuguesa de Qualidade da Água. Diário da República I-A: 5747-5765

Raeva D, Slavov T, Stoyanova D, Zivčič L, Tkalec T, Rode S (2014) Expanded Nuclear Power Capacity in Europe, Impact of Uranium Mining and Alternatives. EJOLT Report No. 12, 129 pp

Teixeira RM, Antunes IMHR, Neiva AMR (2010) Uranium minerals from the Picoto uranium mine area, central Portugal. Geoch Cosmoch Acta 74:A1034

WHO (2011) Guidelines for drinking water quality.4th Ed (Geneva). Available at http://Whqlibdoc.Who.int/publications/2011/9789241548151_eng.pdf

Xuejing X (1995) Analytical requirements in international geochemical mapping. Anal 120:1497-1504