

Potential toxic elements in stream sediments, soils and waters in an abandoned radium mine (central Portugal)

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Received: 18 December 2016 / Accepted: 17 March 2017 / Published online: 25 March 2017
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Abstract The Alto da Várzea radium mine (AV) exploited ore and U-bearing minerals, such as autunite and torbernite. The mine was exploited underground from 1911 to 1922, closed in 1946 without restoration, and actually a commercial area is deployed. Stream sediments, soils and water samples were collected between 2008 and 2009. Stream sediments are mainly contaminated in As, Th, U and W, which is related to the AV radium mine. The PTEs, As, Co, Cr, Sr, Th, U, W, Zn, and electrical conductivity reached the highest values in soils collected inside the mine influence. Soils are contaminated with As and U and must not be

used for any purpose. Most waters have pH values ranging from 4.3 to 6.8 and are poorly mineralized (EC = 41–186 $\mu\text{S}/\text{cm}$; TDS = 33–172 mg/L). Groundwater contains the highest Cu, Cr and Pb contents. Arsenic occurs predominantly as $\text{H}_2(\text{AsO}_4)^-$ and $\text{H}(\text{AsO}_4)^{2-}$. Waters are saturated in goethite, haematite and some of them also in lepidocrocite and ferrihydrite, which adsorbs As (V). Lead is divalent in waters collected during the warm season, being mobile in these waters. Thorium occurs mainly as $\text{Th}(\text{OH})_3(\text{CO}_3)^-$, $\text{Th}(\text{OH})_2(\text{CO}_3)$ and $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$, which increase water Th contents. Uranium occurs predominantly as UO_2CO_3 , but $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{CaUO}_2(\text{CO}_3)_3$ also occur, decreasing its mobility in water. The waters are contaminated in NO_2^- , Mn, Cu, As, Pb and U and must not be used for human consumption and in agricultural activities. The water contamination is mainly associated with the old radium mine and human activities. A restoration of the mining area with PTE monitoring is necessary to avoid a public hazard.

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Keywords Radium mines · Enrichment factor ·
Contamination · Remediation · Central Portugal

Introduction

Mining activity is considered as one of the most potentially harmful anthropogenic activities in the world (Acosta et al. 2011) and its disruptive effects on

the environment have been known for decades. In general, mining activities are associated with waste production and the disposal of mine wastes often produces more environmental problems than the mining operations themselves (e.g. Fernandez-Caliani et al. 2009).

In Portugal, between 1908 and 2001, about 60 radioactive ore deposits were extracted for the production of radium and uranium (Carvalho 2014). Following closure, the Portuguese mines were abandoned and local areas of former radium and uranium mines were studied for environmental radioactivity, metals and public health impact (e.g. Pinto et al. 2004; Antunes and Albuquerque 2013; Carvalho et al. 2013; Carvalho 2014; Neiva et al. 2014, 2015, 2016a).

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 tailing dumps in abandoned uranium mining and processing sites pose contamination risks to environment and human health (e.g. Albuquerque and Antunes 2015; Neiva et al. 2016a, b) with a significant amount of potentially toxic elements (PTEs) (Acosta et al. 2011; Favas et al. 2011). PTEs may be transferred from mining areas to nearby stream sediments, soils and waters by drainage and/or atmospheric deposition; thus, abandoned mines are one of the most important sources of contamination (e.g. Siegel 2002; Ferreira da Silva et al. 2004; Boularbah et al. 2006). In recent years, pollution of stream sediments and soils by PTEs in areas adjacent to mine sites has been reported in many countries (e.g. Cui and Xin 2011; Vrhovnik et al. 2013; Neiva et al. 2016b).

The main purpose of this study is to characterize the spatial and temporal geochemistry of selected PTEs in stream sediments, soils, surface water and groundwater associated with the old mine of Alto da Várzea, 65 years after closure. The obtained results will allow assessing the potential toxic contamination and environmental risks associated with the abandoned radium mine and to improve remediation processes in the study area and avoid similar problems in other mine areas.

Alto da Várzea mine area

The Alto da Varzea radium mine (AV mine) area is located at the Central Iberian Zone of the Iberian

Massif (ZCI), located at the southeastern of the town of Guarda (central Portugal) (Fig. 1a). In this area, a Variscan porphyritic two-mica granite occurs and intruded the Beiras Group (previously called Schist-greywacke complex) (EDM 2005). The mine is in a low slope area with altitudes ranging from 810 to 840 m.

The mineralization occurs in quartz veins trending N25–30°E/SW, up to 5 m thick at depth associated with weathered granite and jasper veins. These veins contain secondary U-minerals such as autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{--}12\text{H}_2\text{O}$) and torbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 11\text{H}_2\text{O}$) (EDM 2005).

The mine exploited radium retained in ore minerals and was exploited mainly underground, with three levels at 25, 50 and 75 m, respectively, and a gallery at the hillside. The mine exploitation occurred between 1911 and 1922 (Enterprise: Minaru Lda) and was closed in 1946. The mine area was not restored and actually a commercial area is deployed.

The Alto da Várzea area is characterized by a warm and temperate climate with a Csb type, according to the Köppen and Geiger classification (IPMA 2015). The average annual precipitation is 892 mm. There is more rainfall in winter than in summer, with a gap of 236 mm rainfall between the driest month and the wettest month. The wet season starts in October and lasts until May and the mean annual temperature is 10.7 °C. In August, the hottest month of the year has an average temperature of 39.4 °C, while in January is about 3.5 °C, according to the data of the Guarda weather station, central Portugal (SNIRH 2009).

The hydrology of the area is dominated by the Diz stream that is an effluent of the right bank of Côa river, belonging to the catchment area of the Douro river. The surface drainage runs to SE towards the Diz stream which has a very low water flux in the summer. One dump retained the waste from the mine exploration and contained about 2000 ton of leached materials without any compaction.

The area has rural characteristics and is covered by vegetation, consisting mostly of oaks, pasture and agricultural zones, located around the old mine. The industry is reduced; however, the waste water treatment plant is not efficient and uncontrolled domestic and industrial discharges wastes are an important source of the Diz river contamination.

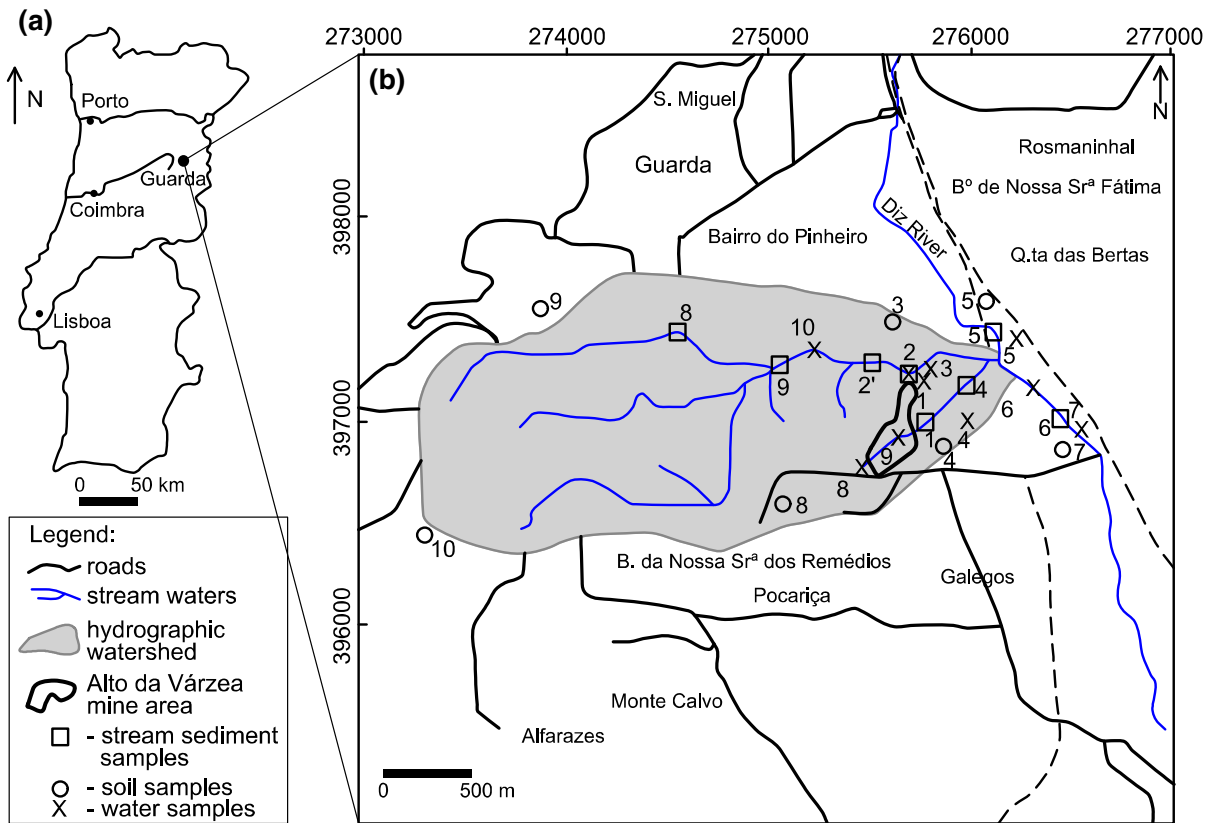


Fig. 1 **a** Location of the Alto da Várzea (AV) radium mine on the map of Portugal; **b** hydrographic stream watershed and location of soil, stream sediment and water sample sites

Material and methodology

A total of 8 stream sediment samples, with 2 of them upstream and 6 downstream of the Alto da Várzea radium mine area were collected. A total of 7 soil samples was also collected, including 2 from an adjacent area outside the mine influence and 5 from inside the area that received the mine influence. The soil samples were collected at a depth between 20 and 30 cm in April 2009. Stream sediments and soil samples were collected in a granitic bedrock. The samples were transported in polyethylene bags, dried at 40 °C, disaggregated with a rubber hammer and sieved through a 2 mm nylon sieve. The pH was measured in a solid-water suspension with a liquid/solid ratio of 2.5. The electrical conductivity (EC) was measured in a liquid/solid rate of 1/5. The <250 µm fraction of stream sediment and soil

samples were digested with *aqua regia* (3:1 HCl-HNO₃), filtered through a 2 µm filter and analysed by ICP-OES, using a Horiba Jobin–Yvon JY-2000 2 spectrometer with a monochromator to determine metals and metalloids. The certified sewage sludge-amended soil BCR 143R was used to validate an internal reference soil, prepared with *aqua regia*. A laboratory standard and duplicate blanks were included at the beginning and the end of 15 analysed samples. The accuracy and precision were determined using the same methodology for water samples. The obtained results were accepted if they were lower than those shown in Table 1. The detection limits in mg/kg are 0.83 for As, 1.7 for Sb, 2.6 for Sr, 2.8 for Th, U and W, 3.0 for Cr and Ni, 3.2 for Fe, 3.3 for Mn, 3.5 for Cd, 3.6 for Co, 4.0 for Al and Pb, 4.1 for Cu and 4.9 for Zn. All the data were obtained at the Department of Earth Sciences, University of Coimbra, Portugal.

Table 1 Allowance of accuracy and precision for routine analysis

Concentration range	Accuracy	Precision
	$\Delta \lg C = \lg \bar{C}_i - \lg C_s $	$\lambda = \sqrt{\frac{\sum_{i=1}^n (\lg C_i - \lg C_s)^2}{n-1}}$
Water		
<3 Detection limit	≤0.29	0.43
>3 Detection limit	≤0.12	0.16
Stream sediment and soil		
<3 Detection limit	≤0.067	0.062
>3 Detection limit	≤0.042	0.059

\bar{C}_i , the average determined value of the standards Relacre_i for water and BCR_i for stream sediment and soil; C_i , the determined value of the standards Relacre for water and BCR for stream sediment and soil; C_s , the recommended value of the standards Relacre for water and BCR for stream sediment and soil; n , number of standard subsamples located within each batch of samples

Cation exchange capacity (CEC) and organic matter (OM) were determined in 3 representative stream sediment samples and 3 soil samples (upstream the mine influence and downstream the mine influence), with the highest U and Th concentrations, at the Department of Soils and Plants, University of Trás-os-Montes and Alto Douro (UTAD), Portugal. CEC was determined according to the method of Thomas (1982). It is the sum of extractable bases and extractable acidity by the ammonium acetate solution (pH7) with a precision of 0.4%. The organic carbon content was determined using an elemental analyzer. CO₂ was quantified by an NIRD (near infrared detector), after oxidation at 1100 °C, and CO₂ was converted into C. Assuming that OM contains 58% organic carbon (Nelson and Sommers 1996), the organic matter (OM) was calculated applying a factor of 1.724 to the C. The precision was of 1.8%.

The grain size distribution and textural characteristics were obtained in the same 3 stream sediment and 3 soil samples, where CEC was determined, at the Department of Earth Sciences, University of Coimbra, Portugal. The grain distribution of the fraction <2 mm of these samples was obtained by laser diffraction analysis, with a Coulter laser granulometer (2 mm–0.04 μm) with a precision up to 5%. The mineralogical identification of clay minerals in the <2 μm fraction in oriented samples, before and after treatments with ethylene glycol and heating up to 550 °C, was carried out with a Philips 3710 X-ray diffractometer, with a Cu tube, at 40 kV and 20 nA.

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 AV8, AV6 and AV9). These nine water samples are considered inside 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). Water samples 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 HNO₃ acidified samples with (pH 2), while anions were determined in non-acidified samples by ion chromatography (Dionex ICS 3000 Model). The detection limits in μg/L 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 NO₂⁻; 1.37 for NO₃⁻; 2.27 for SO₄²⁻ and 1.19 for PO₄³⁻. 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, and the calculations were taken according to defined methodologies (Xuejing 1995; Min et al. 2014). 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 less than $\pm 10\%$ for most water samples.

The modelling of As, Pb, Th and U in water samples with the highest concentrations of these elements was carried out using the software Phreeq C and the ThermoChimie database (Andra 2009; Parkhurst and Appelo 2013).

Results and discussion

Geochemistry of stream sediments and soils

The textural characteristics, physical–chemical parameters, and concentrations of PTEs in stream sediments from the old Alto da Várzea radium mine area are given in Table 2a. The stream sediments contain mainly sand. The clay size fraction ($<4 \mu\text{m}$) is up to 2.7%. The $<2 \mu\text{m}$ clay size fraction contains illite, kaolinite and vermiculite. The pH values are of 5.8–6.8 in upstream sediments and 4.2–6.6 in downstream sediments (Table 2a). The electrical conductivity (EC) ranges from 54 to 107 $\mu\text{S}/\text{cm}$ in upstream sediments and ranges between 28 and 243 $\mu\text{S}/\text{cm}$, but presents only one value of 499 $\mu\text{S}/\text{cm}$ in downstream sediments, suggesting that the contamination is low. The CEC values are of 2.1–2.5 and 9.6 cmol/kg in upstream and downstream sediments, respectively. The OM values are also low of 0.31–0.93% in upstream sediments and 2.8% in downstream sediments.

In general, the downstream sediments have higher Fe, As, Pb, U and W concentrations than the upstream sediments (Fig. 2; Table 2a) due to erosion and leaching of the mine dumps. The OM content and clay size fraction of stream sediments are low to have retained any significant concentration of PTEs. The Fe concentration is up to 25.0 g/kg. Probably As, Pb and U are adsorbed by Fe-oxyhydroxides, as in other uranium mine areas (e.g. Pinto et al. 2004; Cabral Pinto et al. 2008, 2009; Carvalho et al. 2012; Larios et al. 2012).

The physical–chemical parameters and concentration of PTEs of soils from the old Alto da Várzea

radium mine area are presented in Table 2b. The soils are dominantly cambisols (Cardoso et al. 1973) and were not considered evolved soils. However, these soils are suitable for pasture and forest occupation and/or agricultural potential (European Environment Agency 2006).

The soils present similar textural characteristics as stream sediments. The soils contain mainly fine-sand and the clay size fraction ($<4 \mu\text{m}$) is up to 8.5%. The $<2 \mu\text{m}$ clay size fraction contains illite, kaolinite and vermiculite. The soils from the study area have a local agricultural activity but in general, presented a lower OM content (up to 3.12%). The CEC values are of 4.0–4.8 and 10.2 cmol/kg in soil samples collected outside and inside mine influence area, respectively (Table 2b).

These soils are neutral to acidic with values of 4.9–5.0 and 4.9–5.7 in soil samples collected outside and inside the mine influence, respectively, mainly due to the influence of the granite. Metals are more mobile and more available in more acid than neutral conditions (Alloway 1995).

The maximum concentrations of PTEs—As (130 mg/kg), Co (6.3 mg/kg), Cr (22.6 mg/kg), Mn (956 mg/kg), Sb (5.0 mg/kg), Sr (19.2 mg/kg), Th (118 mg/kg), W (17.4 mg/kg) and Zn (141 mg/kg) are higher in soil samples from inside mine influence than in the soil samples from outside this influence (Fig. 3; Table 2b). These soils collected inside mine influence contain the highest EC (171 $\mu\text{S}/\text{cm}$), because PTE were released from the mine dumps and retained in the closest soils. Otherwise, Fe and Mn concentrations in soils collected inside mine influence were within the range measured in the background soil samples but with the highest maximum contents (Table 2b). CEC is related to the amount of Fe and Mn hydroxides of soils (Forghani et al. 2015), which played an important adsorption role in the studied soils, as clay minerals occur in a small amount (Table 2b).

Geochemistry of surface water and groundwater

The abandoned mining area is located close to a rural area, and some of its water is used for agricultural irrigation. Physical–chemical parameters and chemical analyses of water samples from the studied area are given in Table 3. The water sample AV1 was collected just in January 2008, because after that the area was remobilized and this water point disappeared.

Table 2 Textural characteristics, physical–chemical parameters, potential toxic elements (PTE) of stream sediments and soil from the old Alto da Várzea (AV) radium mine area

Textural characteristics		Physical–chemical parameters				PTE (mg/kg), except Al and Fe (g/kg)																
% sand	% silt	% clay	pH	EC S/cm	CEC cmol/kg	OM %	Al	Fe	As	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sr	Th	U	W	Zn	
<i>(a) Stream sediments</i>																						
Upstream																						
SD8	96.9	2.7	0.41	6.8	107	2.5	0.93	15.5	12.1	54.5	*	4.5	8.5	275	5.4	11.7	4.3	5.8	103	49.7	10.5	69.4
SD9	99.1	0.67	0.19	5.8	54	2.1	0.31	12.1	11.8	41.3	*	11.7	16.4	174	6.0	19.0	3.2	7.6	88.0	34.8	5.9	107
Downstream																						
SD1	nd	nd	nd	5.8	71	nd	nd	15.1	9.7	43.8	*	*	*	192	*	13.1	*	6.4	62.5	32.1	5.4	91.5
SD2	83.1	14.2	2.7	6.2	195	9.6	2.8	14.9	15.5	51.5	4.8	4.0	8.4	3727	4.7	19.3	*	11.9	385	668	35.1	64.5
SD2 ⁺	nd	nd	nd	6.4	243	nd	nd	23.4	24.2	109	4.8	51.6	23.4	8671	21.9	81.1	*	2.7	168	575	14.9	109
SD4	nd	nd	nd	6.6	28	nd	nd	21.5	22.4	67.9	4.7	7.8	13.7	466	6.0	27.1	3.8	14.1	89.3	51.8	12.7	102
SD5	nd	nd	nd	4.2	60	nd	nd	24.0	25.0	60.9	*	4.0	8.9	125	*	24.1	5.5	7.2	44.6	55.4	4.8	42.1
SD6	nd	nd	nd	4.3	499	nd	nd	12.5	13.1	41.6	3.8	11.7	15.3	190	5.6	13.3	*	7.8	92.0	41.4	26.3	107
<i>(b) Soils</i>																						
Inside the mine influence																						
SL9	64.9	26.6	8.5	5.3	47	4.8	1.47	37.4	20.9	110	6.2	9.8	8.5	551	7.4	34.1	3.4	13.1	117	82.4	11.5	92.7
SL10	80.3	16.1	3.5	4.9	29	4.0	3.12	25.8	12.7	123	*	9.5	29.7	412	4.2	40.3	2.9	6.7	56.9	162	6.5	65.2
Outside the mine influence																						
SL3	nd	nd	nd	5.5	171	nd	nd	28.2	17.7	130	5.8	22.6	17.1	956	4.9	32.3	2.0	19.2	70.8	125	11.7	141
SL4	nd	nd	nd	4.9	150	nd	nd	28.4	15.5	92.6	3.8	7.7	10.2	208	6.6	37.8	5.0	12.8	84.3	69.9	7.7	70.9
SL5	nd	nd	nd	5.1	108	nd	nd	17.2	11.1	67.9	*	3.6	17.8	317	3.4	17.0	*	7.5	54.0	41.3	6.5	*
SL7	78.0	19.2	2.8	5.3	107	10.2	42.8	13.8	10.0	99.4	6.3	11.4	11.5	472	6.1	30.8	2.2	14.8	117	77.9	17.4	93.0
SL8	nd	nd	nd	5.7	77	nd	nd	36.7	19.4	105	6.1	9.6	12.1	301	6.6	39.8	2.2	15.6	118	77.2	6.6	103

EC electrical conductivity, CEC cation exchange capacity, OM organic matter, nd not determined, * below the detection limit, Cd was not detected, Analyst: A.C.T. Santos

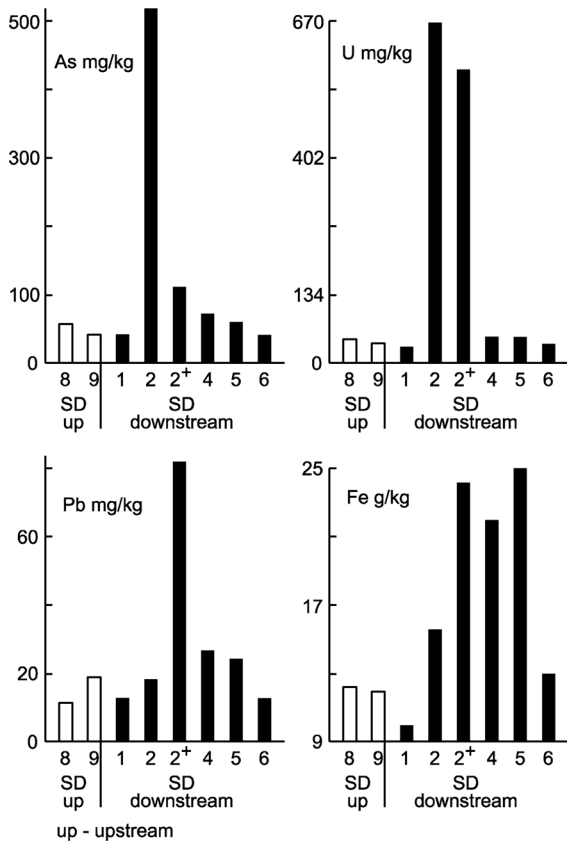


Fig. 2 Arsenic, U, Pb and Fe concentrations in stream sediments (SD) from upstream and downstream of the Alto da Várzea radium mine

In general, the water collected inside mine influence contains the highest NO_2^- , SO_4^{2-} , PO_4^{3-} , HCO_3^- , Na, K and PTEs concentrations than the local background due to erosion and leaching of the mine dumps (Table 3). The water carried the PTEs and is responsible for the transport of contamination off-site (Larson et al. 2012). However, there are no significant differences between water sample collected outside mine influence (water sample AV10) and the water samples located inside the mine influence area (Table 3).

The pH values ranged from 4.3 to 6.8 with more acidic values during summer than winter. The acidic waters resulted of sulphides oxidation from the mineralized veins and consequently from tailings and dumps. The acidic water formed by the oxidation of sulphides is corrosive and causes the leaching of PTEs (e.g. Ca, Mg, Al and Li) and F^- from the host

rocks (Antunes et al. 2016). The Eh values vary from 197 to 476 mV. Most waters are poorly mineralized ($\text{EC} = 41\text{--}209 \mu\text{S/cm}$), which was also supported by the total dissolved solids (TDS), ranging from 33 to 172 mg/L. The highest EC and TDS occur in a stream water (water sample AV6: $\text{EC} = 636 \mu\text{S/cm}$ and $\text{TDS} = 352 \text{ mg/L}$) and in a well (water sample AV7: $\text{EC} = 397 \mu\text{S/cm}$ and $\text{TDS} = 236 \text{ mg/L}$), which receives drainage from domestic and agricultural activities.

In general, stream waters reach higher CE values, Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , HCO_3^- , Ca, Mg, Na, K, Fe, Mn, Zn, TDS and TS contents than groundwaters (wells and spring), because they are the most influenced by the seasonal climate conditions and domestic and agricultural activities. However, groundwater samples contain the highest Cu (up to $77.2 \mu\text{g/L}$; sample AV5), Cr (up to $8.2 \mu\text{g/L}$; sample AV4) and Pb (up to $50.7 \mu\text{g/L}$; sample AV5) contents which could be related to the dissolution from underground mineralized quartz veins. There are no significant differences in As (up to $32.8 \mu\text{g/L}$; sample AV7), Th (up to $4.9 \mu\text{g/L}$; sample AV7 and AV8) and U (up to $57.7 \mu\text{g/L}$; sample AV7 and AV6) contents from surface water and groundwater (Table 3). However, in general, the water from a spring (AV5) is the poorest mineralized water containing the lowest range EC value ($41\text{--}58 \mu\text{S/cm}$) and Cl^- ($6.3\text{--}9.4 \mu\text{g/L}$), NO_2^- ($0.35\text{--}0.91 \mu\text{g/L}$), NO_3^- ($0.06\text{--}1.2 \mu\text{g/L}$), SO_4^{2-} ($1.1\text{--}1.5 \mu\text{g/L}$), HCO_3^- ($6.6\text{--}10.4 \mu\text{g/L}$), Ca ($1.0\text{--}1.4 \mu\text{g/L}$), Mg ($0.39\text{--}0.59 \mu\text{g/L}$), Na ($5.2\text{--}6.1 \mu\text{g/L}$), K ($0.52\text{--}0.74 \mu\text{g/L}$), Mn ($7.4\text{--}11.5 \mu\text{g/L}$), Ni ($0.4\text{--}7.1 \mu\text{g/L}$), Sr ($6.6\text{--}11.5 \mu\text{g/L}$), As ($1.3\text{--}13.5 \mu\text{g/L}$) and U ($1.3\text{--}55.0 \mu\text{g/L}$) contents but the highest Al (up to $85.4 \mu\text{g/L}$), Li (up to $13.0 \mu\text{g/L}$) and Pb (up to $50.7 \mu\text{g/L}$) contents (Table 3).

Most water samples have low metal concentrations and are classified as neutral-metal poor to acid-metal poor (Fig. 4). According to the Piper classification, most water samples were of undefined type or Na-HCO_3^- type. The water from mine gallery (AV2) tends to present the highest contents of F^- (up to 0.31 mg/L), Li (up to $58 \mu\text{g/L}$), Mn (up to $1450 \mu\text{g/L}$) and U (up to $66 \mu\text{g/L}$) (Table 3). In general, there is an increase in U water contents in April and July 2009 due to evaporation and lower U contents during January 2009, probably due to a dilution effect. There is not a significant seasonal variation in the major ion concentrations and PTEs (Table 3). There are no

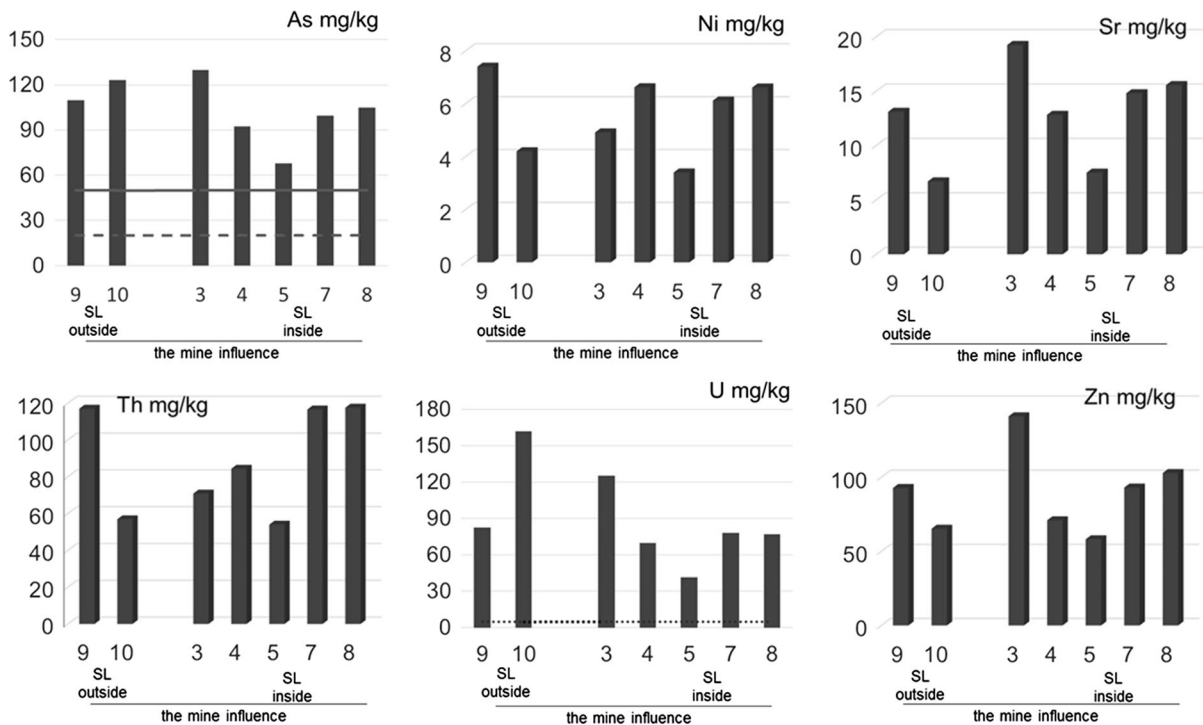


Fig. 3 Selected values of potential toxic elements of soils collected outside mine influence (SL up) and outside the influence (SL downstream) of the Alto da Várzea radium mine. Maximum values for *dashed lines* public, private green areas

and residential sites; *solid lines* industrial areas (Decreto Ministeriale 1999); *dotted lines* U contamination value (Ribera et al. 1996)

significant differences in As, Th and U contents from surface water and groundwater.

Water compositions from Alto da Várzea mine area was plotted in the Eh–pH for the system As–Fe–O–H–S and all samples fall in the H_2AsO_4^- field stability because they have a similar range for Eh and pH values (Fig. 5).

Speciation of As, Pb, Th and U in surface waters and groundwaters

Arsenic occurs as pentavalent species in waters from old Alto da Várzea mine, mainly as $\text{H}_2(\text{AsO}_4)^-$ (up to 98.46%), but also as $\text{H}(\text{AsO}_4)^{2-}$ (48.75%) (Table 4), the less toxic and mobile form of arsenic (Hughes et al. 2011). It also formed small proportions of calcium-arsenic complexes $\text{Ca}(\text{HAsO}_4)$ (up to 1.40%) in some waters (AV2, AV7 and AV6), due to their high Ca

concentrations (Table 3). The waters AV10 (April 2009), AV1 (July 2009), AV2 (April 2009), AV7 (April and July 2009) and AV6 (July 2009) are saturated in ferrihydrite, goethite, haematite and lepidocrocite. Pentavalent arsenic has high affinity to be adsorbed by oxyhydroxides, which reduces its mobility in solution (Mamindy-Pajany et al. 2009). Waters AV10 (July 2009) and AV2 (July 2009) are saturated in crystalline Cr_2O_3 (cr), goethite and haematite. AV7 and AV5 (in July 2009) are also saturated in Cr_2O_3 . AV1, AV7 and AV6, all of them collected in July 2009, are also saturated in trevorite (NiFe_2O_4).

Lead mainly occurs as divalent form in water samples AV10, AV2 and AV5 all of them collected in July 2009, due to their pH values lower than 6.0 (Tables 3, 4). In these waters the mobility and bioavailability of Pb is high. However, in some waters (AV2, AV7, AV6 in April 2009), PbCO_3 (up to

Table 3 Physical–chemical parameters and chemical results of water samples from the old Alto da Várzea (AV) radium mine area

Sample	Date	Physical–chemical parameters						Anions (mg/L)						Major cations (mg/L)			
		T (°C)	pH	Eh (mV)	DO (mg/L)	EC (µS/cm)	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	HCO ₃ ⁻	Ca	Mg	Na	K
AV10																	
a	July 2008	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
b	January 2009	5.9	6.1	237	1.2	142	0.13	31.6	0.64	11.9	27.2	0.10	21.6	14.3	3.1	19.9	3.7
c	April 2009	10.3	5.9	244	7.4	123	0.10	18.6	0.70	4.6	23.8	0.03	28.6	11.5	2.7	15.0	2.8
d	July 2009	14.4	4.7	389	1.8	135	0.19	10.0	0.76	0.73	10.1	*	60.0	10.9	2.4	13.0	2.7
AV1																	
a	July 2008	18.8	6.5	216	11.7	69	0.11	5.7	3.5	3.5	*	0.27	30.6	5.9	1.79	7.2	4.2
AV2																	
a	July 2008	13.4	6.5	223	5.2	104	0.24	5.1	2.0	0.06	0.79	*	49.6	13.5	3.7	5.6	1.23
b	January 2009	10.6	6.3	225	1.0	101	0.23	5.3	1.75	0.05	2.3	*	62.0	12.3	3.2	4.9	1.20
c	April 2009	12.3	6.3	221	7.8	101	0.24	6.5	1.51	0.48	3.5	*	54.0	14.2	3.6	5.9	1.31
d	July 2009	15.3	5.1	373	5.4	127	0.31	5.8	1.30	0.11	3.2	*	80.7	15.5	3.6	6.1	1.29
AV3																	
a	July 2008	16.6	5.8	257	2.7	143	0.17	16.6	1.18	6.2	13.1	0.06	38.6	12.2	2.8	14.3	4.2
b	January 2009	6.0	6.2	230	1.2	139	0.11	25.3	0.62	11.1	24.3	0.07	21.6	14.5	3.2	17.8	3.7
c	April 2009	9.9	5.8	254	5.1	127	0.16	17.9	0.66	6.1	22.7	*	26.0	12.1	3.0	14.3	3.2
d	July 2009	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AV4																	
a	July 2008	14.6	5.6	257	3.1	111	0.08	14.6	0.92	0.63	17.0	0.12	25.0	8.8	2.2	12.4	2.0
b	January 2009	7.7	5.7	258	0.78	104	0.11	15.1	0.69	2.8	24.1	0.11	18.4	8.9	2.3	12.8	1.78
c	April 2009	11.1	5.3	282	2.4	115	0.10	14.6	0.70	7.9	20.6	0.07	22.6	10.3	2.5	13.3	2.1
d	July 2009	14.5	4.3	476	2.6	139	0.10	16.0	0.45	0.51	17.8	0.08	29.0	8.2	1.77	12.9	2.1
AV7																	
a	July 2008	18.6	6.4	226	1.3	310	0.05	44.3	2.4	3.2	4.9	1.90	107	15.7	2.4	47.1	12.9
b	January 2009	8.9	6.8	197	0.50	319	0.19	64.2	2.3	3.2	10.5	2.84	117	13.8	2.2	66.0	15.1
c	April 2009	10.9	6.7	201	3.1	280	0.14	47.7	2.0	8.0	14.3	2.32	88.8	13.6	1.85	55.1	12.9
d	July 2009	20.0	6.2	340	2.3	397	0.16	45.1	0.77	4.1	6.7	2.35	146	18.1	2.7	50.7	15.0
AV5																	
a	July 2008	21.0	5.5	275	9.4	43	0.22	7.9	0.79	0.06	1.24	0.13	10.0	1.05	0.39	5.2	0.74
b	January 2009	9.0	5.6	264	0.63	41	0.16	6.3	0.91	1.17	1.14	0.14	10.4	1.26	0.51	5.2	0.64
c	April 2009	10.9	5.3	278	6.1	48	0.15	9.4	0.68	1.11	1.30	0.10	8.0	1.35	0.59	6.1	0.60

Table 3 continued

Sample	Date	Physical–chemical parameters										Anions (mg/L)										Major cations (mg/L)				
		T (°C)		pH	Eh (mV)	DO (mg/L)	EC (µS/cm)	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	HCO ₃ ⁻	Ca	Mg	Na	K								
d	July 2009	16.1	4.3	427	2.9	58	0.14	8.5	0.35	1.11	1.49	0.10	6.6	1.21	0.51	5.8	0.52									
AV6																										
a	July 2008	23.0	6.8	201	0.80	636	0.25	68.6	2.4	*	32.0	52.5	158	17.6	5.9	85.8	33.0									
b	January 2009	5.8	5.8	253	1.2	135	0.09	27.8	0.62	12.8	29.2	0.08	19.0	14.2	3.3	17.6	3.5									
c	April 2009	13.9	6.6	203	5.2	298	0.06	46.9	1.63	1.45	33.6	3.4	79.6	15.9	2.1	54.0	14.7									
d	July 2009	22.4	6.3	336	2.0	610	0.10	69.3	0.84	0.36	36.5	13.6	202	20.7	2.8	72.4	21.0									
AV8																										
a	July 2008	22.7	6.4	229	2.5	209	0.20	12.3	2.1	2.4	4.6	3.41	73.6	20.3	3.8	11.8	11.1									
b	January 2009	6.1	6.4	222	1.3	194	0.18	37.8	1.92	4.1	22.7	4.82	56.0	13.5	2.3	34.3	10.7									
c	April 2009	10.4	5.9	247	9.7	133	0.10	18.0	0.70	5.8	21.4	*	35.0	12.9	3.1	16.2	2.9									
d	July 2009	16.7	5.3	340	5.2	112	0.15	12.8	0.44	0.36	8.4	*	34.7	7.8	1.71	10.8	1.44									
AV9																										
a	July 2008	17.2	6.4	226	0.97	142	0.20	12.9	1.89	0.51	2.7	*	66.0	10.7	2.4	13.4	10.7									
b	January 2009	4.8	6.2	233	0.68	101	0.16	19.4	0.93	7.5	11.2	*	34.0	9.7	2.0	13.8	4.7									
c	April 2009	12.3	6.4	217	9.0	98	0.11	11.7	0.72	5.8	10.6	*	28.2	8.0	2.0	10.4	3.9									
d	July 2009	16.3	4.7	378	2.7	186	0.17	14.2	0.82	0.51	3.9	*	76.9	12.0	2.1	13.6	10.2									
VMR							1	70	n.d.	50	575	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.									
VMA							15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.									
VP							1.5	250	0.5	50	250	n.d.	n.d.	n.d.	n.d.	200	n.d.									
Sample	Trace elements (µg/L)																									
	Al	B	Ba	Cd	Co	Cu	Cr	Fe	Li	Mn	Ni	Pb	Sr	Zn	As	U	Th	TDS	TS							
AV10																										
a	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–							
b	*	30.2	21.6	*	2.1	*	*	*	*	8.7	*	*	65.0	4.1	11.4	1.01	2.8	129	177							
c	*	32.1	9.6	*	*	*	*	11.5	*	12.2	*	*	38.8	*	11.4	55.0	4.2	104	105							
d	22.0	32.7	17.2	*	*	14.5	3.7	66.0	6.9	56.8	3.9	15.8	46.5	15.0	*	55.7	*	114	114							
AV1																										
a	22.3	*	17.5	5.1	5.0	16.9	*	54.6	3.3	80.7	17.5	*	28.3	366	11.8	60.6	3.3	86	90							
AV2																										
a	*	*	8.3	2.6	3.3	*	*	10.6	33.4	1082	2.1	*	29.7	2.7	1.3	38.4	2.8	99	131							
b	*	4.0	3.4	*	3.3	*	*	*	27.3	1072	*	*	23.9	*	15.3	8.1	3.7	89	183							

Table 3 continued

Sample	Trace elements (µg/L)											Solids (mg/L)							
	Al	B	Ba	Cd	Co	Cu	Cr	Fe	Li	Mn	Ni	Pb	Sr	Zn	As	U	Th	TDS	TS
c	1.55	4.7	–	*	*	*	2.3	28.3	28.8	982	5.2	1.56	26.1	13.4	13.2	61.8	*	87	91
d	13.2	18.1	5.3	*	*	28.3	7.2	17.1	58.3	1450	1.40	0.99	36.9	7.2	10.6	66.0	*	102	114
AV3																			
a	*	31.1	17.1	*	*	2.6	*	9.5	0.96	36.7	*	*	45.5	4.2	4.3	35.3	2.3	104	123
b	*	31.4	19.4	*	1.79	*	*	*	*	10.7	3.1	*	52.5	4.0	5.9	3.5	3.1	129	171
c	3.49	36.9	12.1	*	1.70	*	2.8	15.8	*	16.9	*	0.80	39.8	*	16.1	54.3	3.7	112	114
AV4																			
a	*	33.2	20.2	2.4	1.86	2.5	*	6.2	1.10	21.1	5.0	*	37.5	5.4	3.0	31.0	2.2	82	98
b	*	35.2	17.2	*	2.2	2.2	*	*	*	26.8	1.74	*	34.6	4.3	2.3	2.1	1.47	92	107
c	5.2	32.3	16.2	*	*	*	3.3	7.6	*	34.9	1.50	*	37.4	*	17.3	45.7	4.4	115	118
d	27.1	51.1	38.4	*	7.5	41.3	8.2	7.7	7.3	16.1	6.0	8.8	39.7	9.7	1.47	55.9	*	98	99
AV7																			
a	0.18	84.4	7.5	4.3	2.0	2.9	*	16.6	0.82	305	1.9	*	44.0	4.9	22.1	32.2	1.89	215	226
b	*	97.9	–	*	1.73	*	*	21.7	*	248	*	*	35.5	*	30.0	1.51	3.0	236	244
c	*	85.1	3.4	*	*	*	*	89.8	*	87.5	*	27.7	30.6	*	32.8	45.4	4.9	167	237
d	8.0	102	19.5	*	*	13.6	7.0	44.5	7.3	353	10.8	*	60.7	10.9	19.1	57.2	*	203	264
AV5																			
a	3.9	*	7.2	3.0	2.4	*	*	12.2	5.5	10.4	0.40	*	9.5	3.4	1.34	35.3	2.2	33	120
b	*	*	5.6	*	2.4	*	*	*	1.20	7.4	4.0	2.1	6.6	*	9.4	1.28	2.1	33	57
c	66.7	*	4.5	*	1.77	*	*	*	1.51	10.3	*	*	8.0	*	10.2	46.0	3.6	47	50
d	85.4	3.9	28.5	*	*	77.2	3.0	17.3	13.0	11.5	7.1	50.7	11.5	19.0	13.5	55.0	*	50	55
AV6																			
a	6.0	106	6.6	2.7	3.3	*	*	85.9	3.0	69.9	6.8	*	28.6	14.6	9.0	29.6	2.9	114	523
b	*	32.3	20.0	*	*	*	*	3.4	*	5.3	*	*	54.4	5.8	6.2	*	2.3	124	137
c	10.0	81.2	7.6	*	*	*	2.1	130	*	81.4	0.81	1.38	30.6	21.0	20.5	47.8	4.3	223	254
d	47.2	106	17.3	*	*	17.3	5.7	399	13.1	160	2.3	*	52.5	23.3	4.1	57.7	*	352	438
AV8																			
a	6.9	10.0	11.9	*	*	7.2	*	112	2.7	115	4.7	*	47.9	9.3	14.5	32.6	0.74	139	317
b	5.7	51.6	12.5	*	4.4	*	*	36.9	*	65.0	1.14	*	36.2	20.0	10.2	1.83	2.2	172	1313
c	*	40.3	14.0	*	*	*	*	29.4	*	15.5	0.46	*	45.8	*	14.9	53.0	4.9	120	123
d	21.6	27.9	17.6	*	*	9.5	*	91.3	8.8	35.2	*	*	36.9	10.9	7.7	54.1	*	86	97

Table 3 continued

Sample	Trace elements ($\mu\text{g/L}$)													Solids (mg/L)						
	Al	B	Ba	Cd	Co	Cu	Cr	Fe	Li	Mn	Ni	Pb	Sr	Zn	As	U	Th	TDS	TS	
AV9																				
a	*	11.7	17.0	*	*	2.3	*	44.8	1.84	261	2.2	*	44.2	5.5	4.3	33.9	2.5	104	125	
b	*	13.9	15.5	*	3.8	*	*	*	*	120	*	*	36.6	22.7	10.3	*	2.1	94	116	
c	*	10.0	12.5	*	2.5	*	*	248	*	163	2.5	*	30.3	10.1	19.0	51.4	3.6	76	86	
d	9.7	26.8	32.9	*	4.4	19.7	*	148	8.9	420	3.3	11.9	50.5	13.4	21.6	53.9	*	114	167	
VMR	5000	300	1000	10	50	200	100	5000	2500	200	500	500	n.d.	2000	100	n.d.	n.d.	n.d.	n.d.	
VMA	20,000	3750	n.d.	50	10,000	5000	20,000	n.d.	5800	10,000	2000	20,000	n.d.	10,000	10,000	n.d.	n.d.	n.d.	n.d.	
VP	200	1000	n.d.	5	n.d.	2	50	200	n.d.	50	20	25	n.d.	n.d.	10	15	n.d.	n.d.	n.d.	

T temperature, *Eh* relative to field pH electrodes, *DO* dissolved oxygen, *EC* electrical conductivity, *TDS* total dissolved solids, *TS* total solids, *AV10* outside the mine influence area, *AV1* drainage water from a mine dump, *AV3*, *AV4* and *AV7* wells, *AV5* spring, *AV6* *AV8* and *AV9* streams, – not collected, * below detection limit; *n.d.* not defined. *VMR* recommended value for agricultural use, *VMA* permitted value for agriculture, *VP* permitted values for human consumption (Portuguese Decrees 1998, 2007), except for U (WHO 2011). Analyst: A. Rodrigues

67.21%) also occurs in a significant proportion, due to the high pH values. In waters with the highest SO_4^{2-} content and most of them with low pH values, PbSO_4 (up to 3.82%) also formed (Table 4). In general, in waters with pH values higher than 6.0, PbCO_3 (up to 67.21%) and PbOH^+ (up to 1.48%) are also present.

Due to the Na-HCO_3^- type of water and their pH values, most species of Th and U are CO_3 complexes. Thorium occurs predominantly as $\text{Th}(\text{OH})_3(\text{CO}_3)^-$ (up to 64.63%), but also as $\text{Th}(\text{OH})_2(\text{CO}_3)$ (up to 54.91%) and $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (up to 19.06%) in waters AV7 (April 2009), AV10 (April 2009), AV7 (April 2009) (Table 4). In the water of the spring AV5 (April 2009) ThF_2^{2+} is predominant (52.75%), followed by ThF_3^+ (19.77%). Soluble thorium species are not stable under natural pH conditions (5–8) which restricts the mobility of thorium. The carbonate concentration increases the formation of soluble complex of carbonate, and those complexes increase the thorium concentration in water. However, they easily form colloids or precipitates (Kim et al. 2010). Thorium (IV) forms strong complexes with humic and fulvic acids, and its adsorption to organic matter, clays and oxides increase with pH, limiting its mobility and bioavailability. The waters AV10 (April 2009), AV1 (July 2009), AV7 (April 2009), AV5 (April 2009) are saturated in crystalline ThO_2 , which means if the pH values decrease, more Th can be released into solution (Vandenborre et al. 2008).

The uranyl carbonate complex, UO_2CO_3 is the predominant specie in most water samples (up to 91.10%) (Table 4). The bicarbonate complexes $\text{UO}_2(\text{CO}_3)_2^{2-}$ (up to 21.24%) occurs in most waters and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (up to 4.26%) also occurs in AV2 (April 2009), AV7 (April and July 2009) and AV6 (April and July 2009). However, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (up to 45.96%) and $\text{CaUO}_2(\text{CO}_3)_3$ (up to 36.56%) are also present in samples AV7 and AV6 in both campaigns, April and July 2009, due to their high Ca content and near neutral pH. Uranium also occurs as UO_2^{2+} (up to 40.63%) in samples AV2 (July 2009), AV10 and AV5 (in April and July 2009) (Table 4). The uranyl ion is more typical in waters with pH values lower than 5.0 and is higher in spring AV5 (July 2009), which has the lowest pH value (4.3) found in waters from the old Alto da Várzea mine (Table 3).

Fig. 4 Classification of waters from the Alto da Várzea radium mine area in the Ficklin diagram (Ficklin et al. 1992)

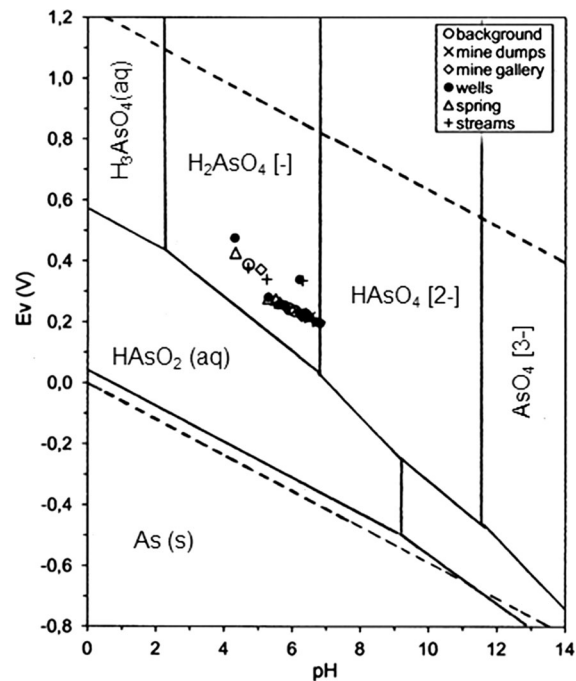
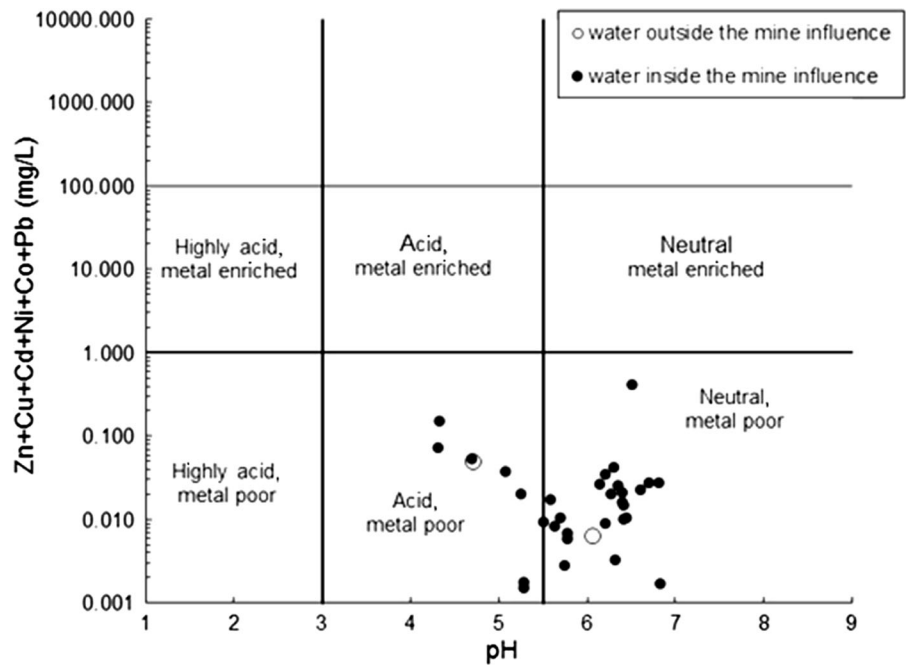


Fig. 5 Eh–pH diagram for the system As–Fe–O–H–S of the waters from the Alto da Várzea radium mine area. Adapted GSJ (2005)

Potentially toxic contamination and relevance to human health

There are several international evaluation methods of PTEs in the sediments and soils, such as Geoaccumulation Index (I_{Geo}), enrichment factor (EF), Potential Ecological Risk Index (PERI) (e.g. Wenyi et al. 1997; Verca and Dolenc 2005).

The degree of contamination caused by PTEs of stream sediments from the old Alto da Várzea radium mine area is classified by the geoaccumulation index I_{Geo} (Müller 1979). The I_{Geo} = log₂[C_n/(1.5, B_n)], where C_n = chemical element concentration (ppm) and B_n = background levels (ppm). The background values for PTE are the median data from a low density geochemical survey of Portuguese stream sediments (Ferreira 2000; Ferreira et al. 2001). The calculated I_{Geo} for upstream and downstream sediments of the studied area are given in Table 5. These sediments are mainly contaminated in As, Th, U and W. The upstream sediments present As belonging to the class 2-moderately contaminated. But As reaches the class 6-extremely contaminated in downstream sediments. The Th, U and W reach the class 4-heavily contaminated in upstream sediments and the class 6 in downstream sediments. Furthermore, Mn reaches the

Table 4 Principal aqueous chemical forms of As, Pb, Th and U in groundwaters and surface waters close to the old Alto da Várzea radium mine predicted by Phreeqc V3.1.5 (Parkhurst and Appelo 1999) and ThermoChimie database

Species names (%)	AV10 April 2009 Outside mine influence	AV10 July 2009 Outside mine influence	AV1 July 2008 Mine dump	AV2 April 2009 Mine gallery	AV2 July 2009 Mine gallery	AV7 April 2009 Well	AV7 July 2009 Well	AV5 April 2009 Spring	AV5 July 2009 Spring	AV6 April 2009 Stream	AV6 July 2009 Stream
H(AsO ₄) ²⁻	-	-	36.58	26.54	2.31	48.75	24.29	3.29	-	43.47	29.64
H ₂ (AsO ₄) ⁻	86.33	-	62.44	72.02	96.69	49.67	74.00	95.81	98.46	54.72	68.31
HAsO ₄ ²⁻	12.72	-	-	-	-	-	-	-	-	-	-
Ca(HAsO ₄)	-	-	-	0.91	-	1.27	1.03	-	-	1.40	1.34
Pb ²⁺	-	93.68	-	59.64	92.43	29.16	-	-	98.42	34.52	-
PbSO ₄	-	3.77	-	-	1.15	1.36	-	-	0.74	3.82	-
PbOH ⁺	-	-	-	1.21	-	1.25	-	-	-	1.48	-
Pb(OH) ₂	-	-	-	-	-	-	-	-	-	-	-
PbCO ₃	-	1.75	-	37.98	5.78	67.21	-	-	-	59.16	-
PbCl ⁺	-	-	-	-	0.32	-	-	-	-	0.89	-
Th(OH) ₃ (CO ₃) ⁻	29.00	-	49.59	-	-	64.63	-	1.21	-	60.65	-
Th(OH) ₂ (CO ₃) ₂ ²⁻	1.99	-	4.22	-	-	19.06	-	-	-	12.91	-
Th(OH) ₂ (CO ₃)	54.91	-	23.92	-	-	19.06	-	9.38	-	22.48	-
Th(OH) ₃ ⁺	7.10	-	11.17	-	-	0.91	-	4.41	-	1.98	-
Th(OH) ₂ ²⁺	1.52	-	-	-	-	-	-	3.35	-	-	-
Th(OH) ₄	1.21	-	10.73	-	-	0.99	-	-	-	1.91	-
ThF ₃ ⁺	1.12	-	-	-	-	-	-	19.77	-	-	-
ThF ₃ ³⁺	-	-	-	-	-	-	-	-	-	-	-
ThF ₂ ²⁺	2.58	-	-	-	-	-	-	2.49	-	-	-
ThF ₄	-	-	-	-	-	-	-	52.75	-	-	-
UO ₂ ²⁺	0.93	-	-	-	-	-	-	6.18	-	-	-
UO ₂ CO ₃	87.98	5.95	-	-	1.86	-	-	10.03	40.63	-	-
UO ₂ (CO ₃) ₂ ⁻	5.64	85.96	57.67	49.52	91.10	8.92	14.88	79.34	41.45	12.44	5.13
UO ₂ (CO ₃) ₃ ⁴⁻	-	0.87	21.24	16.01	3.21	12.03	15.33	-	-	13.57	10.47
CaUO ₂ (CO ₃) ₃ ⁻	1.02	-	-	0.98	-	4.26	1.68	-	-	2.86	1.99
Ca ₃ UO ₂ (CO ₃) ₃	-	-	8.80	17.41	-	45.96	37.77	-	-	41.43	45.82
(UO ₂) ₂ (CO ₃)(OH) ₅ ⁻	1.41	-	3.13	13.75	-	28.59	30.20	-	-	29.37	36.56
UO ₂ OH ⁺	1.44	-	6.80	1.56	-	-	-	-	-	-	-
UO ₂ F ⁺	-	5.79	1.16	-	-	-	-	4.36	2.45	-	-
-, not detected	-	-	-	-	2.33	-	-	5.12	14.42	-	-

-, not detected

Table 5 Geoaccumulation (Igeo) Index for PTEs in upstream and downstream sediments from the old Alto da Várzea (AV) radium mine area

	Al	Fe	As	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sr	Th	U	W	Zn
Upstream															
SD8	0	0	2	0	0	0	0	0	0	1	0	4	4	4	0
SD9	0	0	2	0	0	0	0	0	0	1	0	4	4	3	0
Downstream															
SD1	0	0	2	0	0	0	0	0	0	0	0	4	4	3	0
SD2	0	0	6	0	0	0	3	0	0	0	0	6	8	6	0
SD2 ⁺	0	0	3	0	1	0	4	0	2	0	0	5	8	5	0
SD4	0	0	3	0	0	0	0	0	0	1	0	4	4	5	0
SD5	0	0	3	0	0	0	0	0	0	1	0	3	4	3	0
SD6	0	0	2	0	0	0	0	0	0	0	0	4	4	6	0
	Class														Class

Correspondence between Igeo values and Igeo classes according to Müller (1979)

Igeo ≤ 0 practically uncontaminated	0	2 < Igeo ≤ 3 moderately to heavily contaminated	3
0 < Igeo ≤ 1 uncontaminated to moderately contaminated	1	3 < Igeo ≤ 4 heavily contaminated	4
1 < Igeo ≤ 2 moderately contaminated	2	4 < Igeo ≤ 5 heavily to extremely contaminated	5
		5 ≤ Igeo extremely contaminated	6

Table 6 Enrichment factor (EF) of stream sediments and soils from the Alto da Várzea radium mine area

Sample	Al	Fe	As	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sr	Th	U	W	Zn
Stream sediments															
SD1	1.00	0.74	0.84	0.00	0.00	0.00	0.78	0.00	0.78	0.00	0.87	0.60	0.69	0.60	0.95
SD2	1.00	1.20	9.96	0.00	0.46	0.62	15.38	0.76	1.16	0.00	1.64	3.73	14.64	3.96	0.68
SD2'	1.00	1.19	1.34	0.00	3.76	1.11	22.78	2.27	3.12	0.00	0.24	1.04	8.03	1.07	0.73
SD4	1.00	1.20	0.91	0.00	0.62	0.71	1.33	0.68	1.13	0.65	1.35	0.60	0.79	0.99	0.74
SD5	1.00	1.20	0.73	0.00	0.28	0.41	0.32	0.00	0.90	0.84	0.62	0.27	0.75	0.34	0.27
SD6	1.00	1.21	0.96	0.00	1.59	1.36	0.93	1.08	0.96	0.00	1.29	1.06	1.08	3.54	1.34
Soils															
SL3	1.00	1.13	1.24	1.74	4.23	0.55	2.00	0.98	0.86	1.09	2.06	0.98	1.72	1.38	1.75
SL4	1.00	0.98	1.17	1.14	1.44	0.32	0.43	1.32	1.00	2.65	1.37	1.15	2.21	0.90	0.87
SL5	1.00	1.01	0.79	1.41	1.39	0.21	0.87	1.12	0.68	1.38	1.06	1.21	0.85	1.02	0.87
SL7	1.00	1.30	1.93	3.83	4.36	0.75	2.01	2.49	1.67	2.43	3.23	3.27	2.18	4.18	2.35
SL8	1.00	0.95	1.05	0.98	0.49	0.62	0.37	1.02	0.81	0.89	1.28	1.24	0.81	0.60	0.98

EF = [(element_{sample}/Al_{sample})]/[(element_{baseline}/Al_{baseline})], EF < 2 is deficiency to minimum enrichment, EF = 2–5 is moderate enrichment, EF = 5–20 is significant enrichment, EF = 20–40 is very high enrichment, EF > 40 is extremely high enrichment

class 4 and Pb reaches the class 2-moderately contaminated in downstream sediments. Therefore, downstream sediments are more contaminated than upstream sediments due to erosion and leaching of mine dumps.

The EF was used to assess the enrichment degree and contamination levels of stream sediments and soils from the mine influence area (Table 6) into five classes (Sutherland 2000; Andrew and Sutherland 2004). The EF values were calculated using the Al

concentration as the reference element, because it has a low variation in all stream sediments and soils (average Al contents: stream sediments = 13.8 mg/kg; soils = 21.5 mg/kg; Table 2). Most stream sediment and soil samples from Alto da Várzea mine area present a deficiency to minimum enrichment for all PTEs ($EF < 2$; Table 6). The stream sediment samples—SD2 and SD2'—are the more PTEs enriched samples showing a moderate enrichment in Cr, Ni, Pb, Sr and Th ($EF: 2-5$; Table 6). These stream sediments also have a significant enrichment in As and U ($EF: 5-20$; Table 6) and a very high enrichment in Mn ($EF: 20-40$; Table 6). A stream sediment is also moderately enriched in Cr and W (Sample SD6; Table 6). The EF of soil sample SL7 has a moderate enrichment in all PTE ($EF: 2-5$; Table 6) with exception for Fe and Cu, while soil sample SL3 also has a moderate enrichment in Co, Cr, Mn, Sr, U and Zn. Locally, soil sample SL4 is moderately enriched in Sb and U (Table 6).

The EF of PTEs for stream sediments of Alto da Várzea mine increase in the order: $Mn > U > As > W = Cr = Th > Pb > Ni = Sr > Cu = Zn = Fe = Sb$ and for soil: $Cr = W = Co > Th = Sr > Sb = Ni = Zn = U = Mn = As = Pb > Fe = U$ (Table 6), which is mainly associated with the mineralizations of the area and the mobility degree of each PTE. However, the EF can suggest a source for PTEs of the study area, but cannot indicate its chemical activity and biological availability in stream sediments and soils (Guo et al. 2010).

The Potential Ecological Risk Index (E_f^i) is a parameter of PTE ecological environmental assessment which combines environmental chemistry with biological toxicology and ecology (e.g. Hong et al. 2004; Qinna et al. 2005). The E_f^i index depends on the pollution index (C_f^i) and on the coefficient response for the PTE toxicity (T_f^i) and suggests the hazard of a PTE on the human and aquatic ecosystem, reflecting its toxicity and ecological sensitivity (Guo et al. 2010). The calculated ecological risk level of selected PTEs from stream sediments and soils of Alto da Várzea mine area (e.g. As, Cr, Cu, Ni, Pb and Zn; $E_f^i < 40$) indicates a low ecological risk and a low grade of potential ecological risk ($RI = \sum_f^i < 150$) for these PTEs on the studied area.

The median values of As, Pb, Sb, Th, U, W and Zn of stream sediments from the old Alto da Várzea mine area are higher than those of stream sediments from the European countries (Table 7a). The maximum

concentrations of As, Th and U in stream sediments from the studied area are higher than those of stream sediments from the European countries. The median values of Fe, Co, Cr, Cu, Ni, Th, U and W of stream sediments from Alto da Várzea are higher than those of stream sediments from the old Pinhal do Souto uranium mine area (Table 7a). The maximum values of Fe, As, Cr, Cu, Mn, Th, U and W of stream sediments from the studied area are higher than those of stream sediments from the Pinhal do Souto area. The Alto da Várzea stream sediments only have a higher Sb median value, but higher maximum As, Mn, Sb, Th, U and W concentrations than those of stream sediments from the old Mondego Sul uranium mine area (Table 7a).

There is no Portuguese legislation with the maximum concentrations of PTE accepted in soil. However, a few indicators designed to approximate the quality of soils are currently available (e.g. Varol 2011; Guillén et al. 2012; Kalender and Uçar 2013). In the studied area, soil contamination was assessed as a function of the contamination factor (CF), calculated as the ratio of the PTE concentration to its background concentration (the median between SL9 and SL10 samples). CF has four contaminated degree classes (Håkanson 1980).

In general, almost soil samples from the old Alto da Várzea mine area are moderately contaminated with Al, Fe, As, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sr, Th, U, W and Zn (Table 8). The soil samples collected inside mine influence area are considerably contaminated in Sb and U (SL4) and Cr and W (SL7). However, soil sample SL3 is the most contaminated with a considerable contamination in Mn and Sr and a very high contamination in Cr (Table 8). The contamination in PTE is directly associated with the radium mines of the area.

The PTE concentrations in soils from the Alto da Várzea radium mine area were compared with the maximum accepted soil levels of the Italian Legislation (Decreto Ministeriale 1999), because there is no Portuguese soil legislation. Arsenic contents of soils from the Alto da Várzea radium mine area collected outside and inside the mine influence, indicating that are contaminated with As and must not be used for any purpose (As = 20 mg/kg for public, private green areas and residential sites, As = 50 mg/kg for industrial areas; Fig. 3). This legislation does not give limits for some metals. The U concentrations of all soil

Table 7 Comparison of PTE contents (mg/kg), except Fe (%), obtained by aqua regia digestion of stream sediments and soils from the old Alto da Várzea radium mine area with those of European Countries and two Portuguese uranium mine areas

	Alto da Várzea ^a		European countries ^b		Pinhal do Souto ^c		Mondego Sul inside the mine area ^d	
	Median	Maximum	Median	Maximum	Median	Maximum	Median	Maximum
<i>(a) Stream sediments</i>								
Fe	1.4	2.5	1.96	20	0.83	2.05	3.1	3.8
As	57.7	515	6	231	89.1	194	123	211
Co	1.9	4.8	8	245	0	15.2	12.6	47.4
Cr	6.2	51.6	21	1748	0	21.5	41.4	66.1
Cu	11.3	23.4	14	998	4.3	20.8	30.1	47.4
Mn	234	8671	452	18,898	269	1243	272	1652
Ni	5.5	21.9	16	1201	0	98.4	28.6	53.7
Pb	19.2	81.1	14	4880	37.2	137	51.0	159
Sb	1.6	5.5	0.615	34	3.89	19.6	*	1.87
Sr	7.4	14.1	126	1352	15.34	30.1	7.1	22.3
Th	90.7	385	10	253	32.6	98.4	185	281
U	50.8	575	2*	98	0	35.7	92.1	266
W	11.6	35.1	1.24	82	0	19.8	18.4	26.5
Zn	96.8	109	60	1140	100.4	234	126	346
<i>(b) Soils</i>								
Fe	15.3	20.9	2.0	15.2	8.7	15.1	2.9	6.8
As	10.4	130	6.0	220	94.9	196	112	223
Co	4.8	6.3	7.0	260	0	52.9	9.7	24.6
Cr	9.9	22.6	22.0	2300	1.2	17.3	50.0	76.6
Cu	15.3	29.7	12.0	240	10.4	237	26.9	58.8
Mn	459	956	380	6500	214	6009	89.4	1134
Ni	5.6	7.4	14.0	2600	0	46.1	26.7	60.3
Pb	33.2	40.3	15.0	890	62.2	944	79.8	226
Th	88.1	118	7.2	75.9	26.2	47.2	156	315
U	90.8	162	2.0	53.2	25.1	337	115	377
W	9.7	17.4	<5.0	14.0	19.1	57.2	11.9	29.5
Zn	89.1	141	48.0	2300	92.7	347	124	364

^a The studied area, ^b Salminen et al. (2005), ^c Neiva et al. (2014), ^d Neiva et al. (2016a, b)

samples from Alto da Várzea mine area have higher concentrations than 5 mg/kg (Ribera et al. 1996) and consequently are contaminated in U (Fig. 3). However, almost soils are not contaminated because their PTE contents are below the maximum accepted soil levels.

The median concentrations of Fe, As, Cu, Mn, Pb, Th, U, W and Zn of soils from the Alto da Várzea area are higher than those of median concentrations, respectively, of soils from European Countries (Salminen et al. 2005), but lower than their Co, Cr and Ni median contents. The maximum soils concentration

obtained for Fe, Th, U and W are also higher than, respectively, concentrations of European Countries (Table 7b).

The median values of Fe, Co, Cr, Cu, Mn, Ni, Th and U and the maximum contents of Fe, Cr and Th of soils from Alto da Várzea mine area are higher than those of median values and maximum values contents, respectively, of soils from the old Pinhal do Souto uranium mine area (Table 7b). The median soil values of Fe and Mn and maximum value of Mn from the studied area are higher than those of soils from the Mondego Sul uranium mine area (Table 7b).

Table 8 Contamination factor (CF) of soils from the Alto da Várzea radium mine area

Sample	pH	EC	Al	Fe	As	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sr	Th	U	W	Zn
AVSL3	1	2	1	1	2	2	6	1	3	1	1	1	3	1	2	2	2
AVSL4	1	2	1	1	2	1	2	0	1	2	1	3	2	2	3	1	1
AVSL5	1	1	2	2	1	2	2	0	2	2	1	2	2	2	1	2	2
AVSL7	1	2	1	1	1	2	3	0	1	2	1	2	2	2	1	3	2
AVSL8	1	1	2	2	1	2	2	1	1	2	1	2	2	2	1	1	2

CF = (element_{sample}/element_{background}); CF < 1—low contamination; 1 < CF < 3—moderate contamination; 3 < CF < 6—considerable contamination; CF > 6—very high contamination

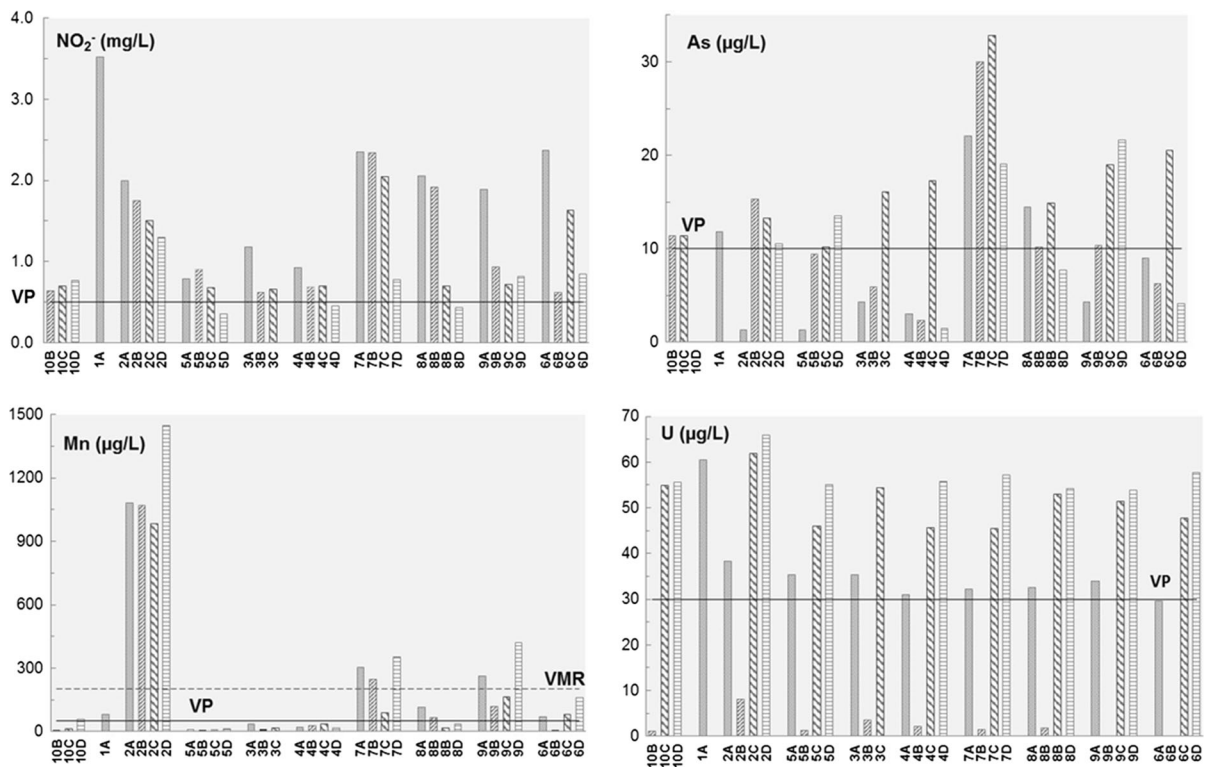


Fig. 6 Seasonal chemical variations in waters from the Alto da Várzea radium mine area. Waters collected during: A July 2008; B January 2009; C April 2009; D July 2009. VMR recommended

values for agriculture, VP permitted values for human consumption (Portuguese Decrees 1998, 2007), except for U (WHO 2011)

To assess the water quality from the Alto da Várzea mine, the guideline values for drinking water quality proposed by the Portuguese legislation (Portuguese Decree 1998, 2007) and the World Health Organization (WHO 2011) were used. Most water samples from the Alto da Várzea mine area are contaminated NO_2^- , Mn, Cu, As, Pb and U and must not be used for human consumption (Fig. 6; Table 3). Iron water contents above 0.3 mg/L

(WHO 2011) will affect the organoleptic water properties which occurred in most water samples from the Alto da Várzea mine area (Table 3). Arsenic is a PTE to human health and mining activities are considered to be one of the sources of As in surface water and groundwater (e.g. Mukherjee et al. 2011; Hiller et al. 2012; Antunes and Albuquerque 2013; Carvalho et al. 2014; Neiva et al. 2014; Antunes et al. 2016).

Some water samples (AV2; AV7 and AV9) are also contaminated in Mn and must not be used for agricultural activities (Fig. 6). All waters present a suspended solids content above the recommended values by Portuguese Legislation (25 mg/L; Table 3) which could be associated with the suspension of Fe oxyhydroxides in waters which was suggested by the turbid water and algae proliferation, particularly in the stream water samples (AV6 and AV8; Table 3). Suspended matter in water affects the quality of aquatic life and causes ecological degradation, increasing the costs of water treatment (Bilotta et al. 2012).

The isotopic Ra^{226} contents of waters associated with the AV mine range between 0.050 and 0.145 Bq/L and are below the legislation defined value (EDM 2005).

Conclusions

The abandoned Alto da Várzea radium mines and associated dumps and tailings, containing the secondary U-minerals autunite and torbernite, are responsible for the stream sediment, soil and water contamination in potentially toxic elements (PTE).

The stream sediments receiving the influence of the mine area contain higher PTE contents than background sediments. These sediments are mainly contaminated in As, Th, U and W. However, they are mainly moderately contaminated in most of PTE because are adsorbed by Fe-oxyhydroxides.

The soils collected inside mine influence, contain the highest EC values and As, Co, Cr, Sr, Th, U, W and Zn, because PTE were released from the mine dumps and retained in the closest soils. Arsenic and U soil contents are above the referenced values of the Italian legislation. Therefore, the soils are contaminated with As and U and must not be used for any purpose. The soils are moderately contaminated with the other PTE, which are below the maximum accepted soil levels, suggesting a low contamination. The contamination in PTE is directly associated with the radium mines of the area.

The waters from the Alto da Várzea mine area are acid to neutral (pH 4.3–6.8) with more acidic values during summer than winter. The acidic waters resulted of sulphides oxidation from the mineralized veins and consequently from tailings and dumps.

Arsenic mainly occurs as pentavalent species ($\text{H}_2(\text{AsO}_4)^-$ and $\text{H}(\text{AsO}_4)^{2-}$), reducing its mobility from waters to soils and stream sediments. The saturation in oxyhydroxides of waters favoured the adsorption of arsenic to these oxyhydroxides, suggesting that the high contents of As in soils and stream sediments are due to the aquatic transport of colloids or by the mechanical transport of arsenic from tailings. Lead is predominantly in divalent form (up to 98.42%), mainly in waters collected in the warm season (July 2009) from outside and inside mine influence. Therefore, Pb has a higher mobility in waters during the summer. PbSO_4 also occurs in waters with a high SO_4^{2-} content and generally in those with the lowest pH values. Thorium occurs mainly as hydroxide-carbonate complexes, due to the Na-HCO_3^- type of waters from Alto da Várzea. Despite these complexes increase the Th concentration in waters by dissolution of ThO_2 , they easily form colloids or precipitated, being unstable in any physical–chemical conditions. If pH values decrease, more Th can be in solution, by dissolution of ThO_2 , in which most waters are saturated. The UO_2CO_3 is predominant in the waters and decreases the mobility of U in waters. However, in waters from the mine gallery and spring with the lowest pH, uranyl ions were formed, increasing their mobility and spreading in the water system.

Most waters are contaminated in NO_2^- , Mn, Cu, As, Pb and U and must not be used for human consumption and some of them in agricultural activities. In general, there is a decrease in U contents from summer to winter, probably due to a dilution effect. There is not a significant seasonal variation in the major ion concentrations and PTEs of the studied waters. All waters present a suspended solid content above the recommended values, affecting the quality of aquatic life and causing ecological degradation.

Arsenic is a PTE to human health and mining activities are considered to be one of the sources of As in stream sediments, soils, surface and groundwater. The obtained results in the studied area reinforce the evidence of environmental and human health risks associated with old abandoned mining areas and the definition and application of adequate remediation methodologies. The contaminated water, stream sediment and soil from the study area must be remediated, such should be suggested to another abandoned radium mines.

Acknowledgements Thanks are due to Prof. João Coutinho for the determination of organic matter and cation exchange capacity in samples of stream sediments and soils and A. Rodrigues for the water analyses, EDM for some information on the Alto da Várzea mine area. This study had the support of Portuguese Fundação para a Ciência e Tecnologia (FCT), through the strategic projects UID/GEO/04035/2013 and UID/MAR/04292/2013 (MARE).

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