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# Spatial and temporal variability of surface water and groundwater before and after the remediation of a Portuguese uranium mine area

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ABSTRACT

The old Senhora das Fontes uranium mine, in central Portugal, consists of quartz veins which penetrated along fracture shear zones at the contact between graphite schist and orthogneiss. The mine was exploited underground until a depth of 90 m and was closed down in 1971. The ores from this mine and two others were treated in the mine area by the heap-leach process which ended in 1982. Seven dumps containing a total of about 33,800 $m^3$ of material and partially covered by natural vegetation were left in the mine area. A remediation process took place from May 2010 to January 2011. The material deposited in dumps was relocated and covered with erosion resisting covers. Surface water and groundwater were collected in the wet season just before the remediation, in the following season at the beginning of the remediation and also after the remediation in the following dry season. Before, at the beginning and after the remediation, surface water and groundwater have an acid-to-alkaline pH, which decreased with the remediation, whereas Eh increased. In general, before the remediation, uranium concentration was up to 83 μg/L in surface water and up to 116 μg/L in groundwater, whereas at the beginning of the remediation it increases up to 183 μg/L and 272 μg/L in the former and the latter, respectively, due to the remobilization of mine dumps and pyrite and chalcopyrite exposures, responsible for the pH decrease. In general, after the remediation, the U concentration decreased significantly in surface water and groundwater at the north part of the mine area, but increased in both, particularly in the latter up to 774 μg/L in the south and southwest parts of this area, attributed to the remobilization of sulphides that caused mobilization of metals and arsenic which migrated to the groundwater flow. Uranium is adsorbed in clay minerals, but also in goethite as indicated by the geochemical modelling. After the remediation, the saturation indices of oxyhydroxides decrease as pH decreases. The remediation also caused decrease in Cd, Co, Cr, Ni, Pb, Zn, Cu, As, Sr and Mn concentrations of surface water and groundwater, particularly in the north part of the mine area, which is supported by the speciation modelling that shows the decrease of most dissolved bivalent species. However, in general, after the remediation, Th, Cd, Al, Li, Pb, Sr and As concentrations increased in groundwater and surface water at south and southwest of the mine area. Before and after the remediation, surface water and groundwater are contaminated in U, Cd, Cr, Al, Mn, Ni, Pb, Cu and As. Remediation caused only some improvement at north of the mine area, because at south and southwest part, after the remediation, the groundwater is more contaminated than before the remediation.



## 1. Introduction

The discharges of uranium and associated radionuclides as well as heavy metals and metalloids from waste and tailing dumps in abandoned uranium mining and processing sites pose contamination risks to surface water and groundwater (Mkandawire, 2013; Skipperud et al., 2013).

In Portugal, there have been about 60 uranium mines exploited during the 20th century for radium and uranium production. These mining and milling activities originated about 13 million tonnes of solid wastes dumped at several sites in the centre-north of the country (Pinto and Silva, 2005; Carvalho et al., 2007). Uranium

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production in Portugal ceased in 2001 and was followed by the approval of an environmental remediation plan for the old and abandoned mine sites (Portuguese Law, 2001).

The effects of abandoned uranium mines on the Portuguese environment have rarely been studied (e.g., Pinto et al., 2004; Antunes et al., 2011; Neiva et al., 2014). Uranium as a heavy metal is chemically toxic and causes a health risk if incorporated in aqueous species (Schöner et al., 2009). The hazard potential of uranium depends on its species and its concentrations. In natural aquatic systems, uranium is stable as U(IV) or U(VI), but depends on redox conditions. U(VI) is more soluble than U(IV) and under neutral and alkaline conditions occurs as $(UO_2)^{2+}$, forming complexes with carbonates, phosphates, vanadates, fluorides, sulphates and silicates (Langmuir, 1997; Cabral Pinto et al., 2008, 2009; Arnold et al., 2011). U(VI) is much more soluble than U(IV) and may migrate as aqueous species in the environment (Arnold et al., 2011). The World Health Organization indicates 15 μg of uranium per litre for drinking water quality (WHO, 2010). Therefore, high concentrations of uranium in water cause a risk for the human health and environment.

Six decades of uranium exploration and mining milling in Europe has resulted in a considerable legacy of waste rock piles, below-grade ore heaps and milling residues disposal sites–Uranium Mine and Mill Tailings (UMMT) (Falck, 2008). The remediation of UMMT sites has two objectives: (1) to interrupt pathways to radiological and non-radiological exposures; (2) to mechanically stabilize the sites against environmental processes, such as erosion (Falck, 2008).

Several studies have shown that remediation processes are long. Many years after the initiation of remediation, metals and metalloids can be re-suspended in water, during hydrological phenomena, because they remain stored in sediments (Galán et al., 2002). In a mining area, recovery can become unpredictable, if high frequency and large spatial ranges are combined (O'Neil, 1998). However, none of the data are available for the effects of remediation in Portuguese mine areas.

The purpose of this study was to characterize the spatial and temporal variability of some chemical proprieties and trace element contents in surface and groundwater before, during and after the remediation of the abandoned Senhora das Fontes uranium mine. These results will allow assessing the impacts of the remediation process and could improve remediation in the study area and avoid similar problems in other mine areas.

## 2. Geology, mineralization and mine site

The old Senhora das Fontes uranium mine area is located in the Sorval village, Guarda County, in central Portugal (Fig. 1a). The Sorval village is at west and the Santa Eufémia village is at north and about 1 km from the mine area. The Póvoa díEl Rei village is located at 2.5 km SW of the mine area (Fig. 1b). Geologically, this area is located in the Central Iberian Zone (CIZ) of the Iberian Massif (Fig. 1a). The schist–greywacke complex (SGC) was intruded by two orthogneisses and a granite and contacts are sharp (Fig. 1b). The syn-F1 medium-grained muscovite-biotite orthogneiss of Senhora das Fontes–Sorval presents a N60–70°W, 80° ± 5S shear foliation given by the orientation of feldspar megacrystals and muscovite. It contains some torbernite and saleeite. This orthogneiss is cut by basic rock veins (Macedo, 1988). The syn-F1 fine-grained muscovite >biotite orthogneiss of Póvoa díEl Rei intruded the SGC and the orthogneiss of Senhora das Fontes–Sorval and the contacts are sharp. It is fine-grained, less deformed and contains more biotite than the other orthogneiss. Its shear foliation is N70W, 80°S and given by the micas orientation, mainly biotite. It is cut by granitic aplite and pegmatite dikes and quartz veins. The syn-F2 medium-grained muscovite granite from Santa Eufémia shows mainly a N75°E orientation of K-feldspar megacrystals, due to a shear deformation. This granite is cut by quartz veins and basic rock veins (Macedo, 1988).

The mine consists of divided quartz veins that penetrated along fractured shear zones, at the contact between graphite schists of the SGC and the Senhora das Fontes–Sorval orthogneiss. However, the mineralization only occurs in E–W fragmented quartz veins up to 1 m thick within the graphite schists. They contain tourmaline, some cassiterite, autunite, $Ca(UO_2)_2(PO_4)_2{\cdot}10–12H_2O$, down to a depth of 40 m. But below, black uranium oxides, uraninite, $UO_2$, and Fe-saleeite, $(Fe,Mg)(UO_2)_2(PO_4)_2{\cdot}8H_2O$ occur in small veinlets or forming elongated nodules cutting the graphite schists of shear zones. The schists support the uranium mineralization, as indicated by radiometric values. The schists are also cut by N45°W, SW long basic rock veins (Fig. 1b) up to 27 m deep and 0.3–0.8 m thick, containing some secondary uranium minerals. This uranium deposit contains a mean of 0.4% $U_3O_8$, reaching 1–2% (Barros, 1966).

At the surface, the uranium deposit had a lense-shaped form of 190 × 10 m dimension (Barros, 1966). It was exploited underground and had three levels reaching the maximum depth of 90 m. The mine was closed down in 1971 and then a small open pit was made by removing the upper mineralized massif. The U was removed from the poor ores of the Senhora das Fontes by the heap-leach process, which consisted of crushing the ore and to add sulphuric acid to dissolve the ore and oxidize the U. This process has taken place in the open pit. The U enriched solution was collected inside the mine. The ores from other Portuguese uranium mines, such as Freixinho and Cótimos were also treated by heap-leach static threshing floors. Ionic exchange was carried out in the area. The heap-leach process ended in 1982.

In the area, there were a closed main well of 90 m depth connected to the three mine levels (Barros, 1966) and also seven main dumps (Fig. 1c). Two of them (A and C) consisted of mud from decantation and waste materials of large dimensions. Another (B) contained precipitates from dissolved wastes. Three others (D, E and F) consisted of waste materials left from the ore dissolution in the open pit. The dump G contained waste materials that came from the opening of the open pit. There was also a small dump associated with the main mine dump. The dumps were partially covered by vegetation.

A remediation took place approximately during one year from May of 2010 to January of 2011. Wells and chimneys were closed. The old structures and buildings were removed. The material deposited in dumps of about 33,800 $m^3$ volume was relocated to be together and covered with erosion resisting covers.

The Senhora das Fontes area is not mountainous, as the altitudes range between 605 m at west and 651 m at southeast of the old mine area. The climate is of maritime temperature. The annual precipitation was 466.8 mm in 2010 and 137.8 mm in 2011. Rainfall dominates during the wet season and was about 115.0 mm in November of 2009–February of 2010 and about 25 mm in the dry season, in May–June of 2010 and 2011, according to the data of the weather station from Pinhel, Guarda, northeast Portugal (SNIRH, 2012). The annual average temperatures ranged from 7 °C to 21 °C, but reached 40 °C in summers and −7 °C in winters. The area has rural characteristics, with dense vegetation, mainly of oaks and pinus and underbrush. Around the old mine, mainly downstream, there are rye fields and pastures. The surface drainage runs to the Massueime stream, which is a tributary in the left bank of the Côa river.

## 3. Water samples and analytical methods

A total of 21 water sampling points including seven streams, ten wells and four springs were chosen to collect water samples