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Alpha Emitting Radionuclides in Drainage from Quinta do Bispo and Cunha Baixa Uranium Mines (Portugal) and Associated Radiotoxicological Risk

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Abstract Two large uranium mines, Quinta do Bispo and Cunha Baixa, district of Viseu, North of Portugal, were exploited until 1991. Sulfuric acid was used for in situ uranium leaching in Cunha Baixa mine and for heap leaching of low grade ores at both mines. Large amounts of mining and milling residues were accumulated nearby. Since closure of mines, the treatment of acid mine waters has been maintained and treated water is released into surface water lines. Analysis of radionuclides in the soluble phase and in the suspended matter of water samples from the uranium mines, from the creeks receiving the discharges of mine effluents, from the rivers and from wells in this area, show an enhancement of radioactivity levels. For example, downstream the discharge of mine effluents into Castelo Stream, the concentrations of dissolved uranium isotopes and uranium daughters were up to 14 times the concentrations measured upstream; ^{238}U concentration in suspended particulate matter of Castelo Stream reached 72 kBq kg^{-1}, which is about 170 times higher than background concentrations in Mondego River. Nevertheless, radionuclide concentrations decreased rapidly to near background values within a distance of about 7 kilometers from the discharge point. Enhancement of radioactivity in underground waters was positively correlated with a decrease in water pH and with an increase of sulfate ion concentration, pointing out to Cunha Baixa mine as the source of groundwater contamination. The radiotoxic exposure risk arising from using these well waters as drinking water and as irrigation water is discussed and implementation of environmental remediation measures is advised.

Keywords Uranium mines · Natural radioactivity · Enhanced radioactivity levels

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Exploitation of radioactive ores in Portugal lasted from 1908 to 2001, and took place mainly in the centre-north of the country. The mines at Quinta do Bispo and Cunha Baixa, near the city of Viseu, were amongst the largest ones in the country (Fig. 1). The mine of Cunha Baixa was exploited from 1967 to 1991, in the beginning by underground works and in more recent years as an open pit. Sulfuric acid was used for in situ leaching of uranium in underground works as well as in heap leaching of low grade ores at the surface. Since cessation of mining, the acid water has been pumped out through the main shaft of the mine for neutralization with calcium hydroxide and precipitation of radionuclides. A total of about 0.5 Mtons of ore were extracted from this mine and the millings tailing materials and sludge from acid water treatment were dumped nearby (Nero et al. 2005).

The mine of Quinta do Bispo is located near 2 km West of Cunha Baixa (Fig. 1), and it was exploited as an open pit. Low grade ores were extracted by the heap leaching method near the mine, and acid process waters were discharged into the open pit. About 1.6 Mtons of waste materials including low grade ores, barren gravel, and milling tailings are disposed on surface. Neutralization of acid waters from the open pit has been performed and treated water discharged into surface water lines (Santos Oliveira et al. 2005). Creeks receiving waste waters both from Cunha Baixa and Quinta do Bispo mines drain into the Castelo Stream, a tributary to Mondego River. About

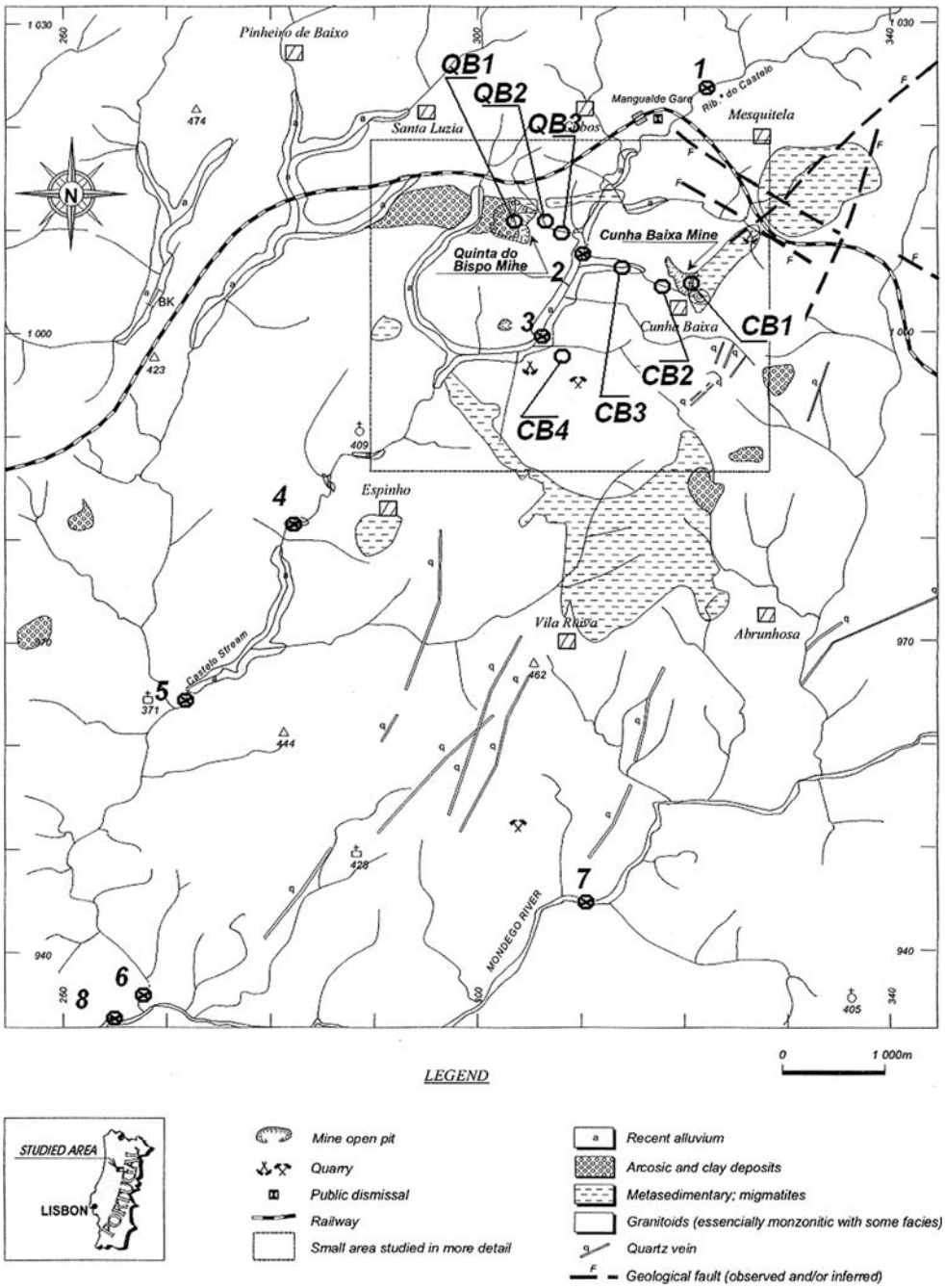

Fig. 1 Map of the area investigated. Sampling stations are indicated with *circles*. *Circles* with a *cross* indicate sampling stations in the Castelo Stream and Mondego River

50 km downstream an artificial lake was built in Mondego River to supply drinking water to the centre of the country.

The radioactive environmental impact of these uranium exploitations was not thoroughly investigated before and the radiological risk to human population and to the environment needs assessment in order to advise decisions on remediation measures (IAEA 2002; Falck 2005). This report gives an account of current levels of environmental radioactive contamination dispersed from these mines into the receiving water bodies.

Materials and Methods

Water samples were collected in May 2002 in this area from uranium mines, creeks, rivers, and wells directly into polyethylene drums and immediately filtered on site. Filtration was performed using membrane nitrate filters with 0.45 μm pore size and 142 mm in diameter. Filtered water was acidified with HNO_3 to pH below 2, and filters with suspended matter were stored for later analysis in the laboratory. Water and suspended matter samples were

analyzed by radiochemical methods and alpha spectrometry as described elsewhere (Carvalho et al. 2005; Oliveira and Carvalho 2006). In brief, known amounts of isotopic tracers (^{232}U, ^{229}Th, ^{209}Po, ^{224}Ra, and stable Pb^{2+}) were added to the samples in the beginning of the chemical processing. For water samples radionuclides were co precipitated with MnO_2 and the precipitate dissolved and passed through ion exchange columns in order to separate the radioelements to quantify. Samples of suspended matter were spiked with the isotopic tracers and completely dissolved with acids before chemical extraction of radioelements by ion exchange column chromatography. Solutions with purified radioelements were then transferred to electroplating cells and radionuclides plated onto stainless steel or silver discs. Radioactivity emitted from the discs was determined with silicon surface barrier low background detectors using an alpha spectrometer OctectePlus (ORTEC EG&G). These methods have been thoroughly tested and limits of detection, accuracy and precision periodically checked with IAEA certified reference materials and through participation in analytical quality assurance intercomparison exercises (Carvalho and Oliveira 2007). Physical chemical parameters of water were measured in situ with a portable multiparameter probe HoribaU-22. Dissolved ions were determined by ion chromatography with a Dionex 500.

Results and Discussion

Radionuclide concentrations in mine waters and in selected examples of surface and well waters are shown in Table 1. In the water from the open pit of Quinta do Bispo mine (QB1), with very low pH = 2.67, ^{238}U concentration was 92,000 mBq L^{-1}, and ^{226}Ra was 1,100 mBq L^{-1}. In the water from Cunha Baixa underground mine (CB1), which has been for several years treated to neutralize the acid, pH still remains low, at 3.48, and ^{238}U and ^{226}Ra concentrations were respectively 2,200 mBqL^{-1} and 84 mBq L^{-1}, much above naturally occurring concentrations in surface waters of the region such as at station Castelo Stream 1 (Table 1).

In Quinta do Bispo mine, after acid neutralization with hydroxide and decantation of the precipitate in ponds, radionuclide concentrations in the creek water receiving pond discharges (QB2, QB3) were much reduced in comparison with untreated water. For example, the concentrations of dissolved ^{238}U and ^{226}Ra were reduced by a factor of 46 and 12, respectively. However, in spite of this treatment, the water in the creek was still acid and contained elevated concentrations of radionuclides (Table 1). In Cunha Baixa, acid water pumped out from the underground mine (CB1) was treated with hydroxide also, decanted in a pond, and the supernatant discharged into a creek flowing into the Castelo Stream. However, especially during summer, this water infiltrates the soil rapidly and largely seeps into the alluvium soil by the Castelo Stream.

Concentration of dissolved radionuclides in Castelo Stream water increased with the discharge of waste waters originated in both mines (Fig. 2). For example, dissolved ^{238}U increased from the naturally-occurring concentration of 15.6 mBq L^{-1} measured at station 1, to 220 mBq L^{-1} at station 3, after receiving drainage from Quinta do Bispo and Cunha Baixa. Further downstream, dissolved uranium concentrations decreased regularly and the enhancement of ^{238}U concentration between station 7 and station 8 in the river Mondego, was from 5 to 7 mBq L^{-1} only. It was noticed that the increase of dissolved uranium in stream water was not accompanied with large increases of ^{226}Ra and ^{210}Po concentrations in the dissolved phase due to differences in the aqueous chemistry of these elements (Fig. 2). This environmental chemistry behaviour of uranium series radionuclides have been described for many others uranium mining sites in various countries (Merkel and Hasche-Berger 2008).

Radionuclide concentrations in particulate matter carried by the Castelo Stream displayed also a strong increase in particulate uranium concentration after the water discharges from the two mines (Table 1). Uranium concentrations were enhanced by a factor of about 4 in the solid phase while the increase was of about 14 in the soluble phase. Concentrations of ^{226}Ra and ^{210}Po in the suspended matter were also enhanced along the Castelo Stream (Fig. 3). The same trend was observed also for ^{230}Th, ^{210}Pb and ^{232}Th radioisotopes that display high sediment-water partitioning coefficients (Kd) and are more associated with the solid phase than uranium and radium (Carvalho et al. 2006, 2007). Nevertheless, a significant decrease in concentrations both in dissolved and in particulate phase was observed during the 7 km of the Castelo Stream from mine discharges to the junction with Mondego River. This decrease occurs as an effect of effluent discharges dilution in the stream and sorption of dissolved radionuclides onto sediments.

In a previous investigation it had been observed that radionuclide concentrations in suspended matter of rivers of this region are positively correlated with radionuclide concentrations in the fine grain size fraction of bottom sediments (Carvalho et al. 2006). Based on these observations, we may infer that the riverbed sediments of Castelo Stream have enhanced radionuclide concentrations also due to the cumulative discharges of waste water from both uranium mines.

The distribution of uranium series radionuclides along surface water lines, and especially along Castelo Stream, is in agreement with the results of geochemical studies performed in the same area focusing stable metals associated to the radioactive ore (Neves et al. 2005; Pereira et al. 2005).

Water from shallow wells located between the Cunha Baixa mine and the Castelo Stream (CB2, CB3, and CB4),

Table 1 Radionuclide concentrations in the dissolved phase and suspended matter of water from the mines of Quinta do Bispo (QB) and Cunha Baixa (CB), irrigation wells, Castelo Stream and Mondego River

	^{238}U	^{235}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po	^{232}Th		
Dissolved (mBq $L^{-1}\pm1\sigma$)									pH	SO_4^{2-}
QB1-open pit	(92.0 ± 4.2)E3	(4.2 ± 0.6)E3	(73.5 ± 3.5)E3	–	(1.1 ± 0.1)E3	(1.2 ± 0.1)E3	87 ± 4	–	2.67	3,645
QB2-water line	(2.2 ± 0.1)E3	110 ± 6	(1.1 ± 0.1)E3	–	92 ± 5	89.2 ± 5.2	40 ± 3	–	3.81	2,495
QB3-water line	679 ± 31	33 ± 2	605 ± 28	–	46 ± 3	11.0 ± 1.2	36 ± 3	–	4.15	2,370
CB1-mine water	(2.2 ± 0.2)E3	106 ± 11	(1.9 ± 0.2)E3	–	84 ± 5	130 ± 6	247 ± 13	–	3.48	1,380
CB2-well	256 ± 11	10.8 ± 0.7	243 ± 11	–	45 ± 8	27 ± 1	21 ± 1	–	5.18	16.0
CB3-well	75 ± 3	3.7 ± 0.3	75 ± 3	–	47 ± 4	32 ± 2	32 ± 1	–	5.26	12.1
CB4-well	415 ± 18	17.7 ± 0.9	392 ± 17	–	61 ± 7	92 ± 7	89 ± 3	–	4.65	461
Castelo stream1	15.6 ± 0.4	0.65 ± 0.04	15.6 ± 0.4		16 ± 3	–	4.6 ± 0.2		5.98	9.1
Castelo stream3	220 ± 10	9.7 ± 0.6	211 ± 9	–	20 ± 2	–	4.5 ± 0.2	–	6.06	599
Castelo stream6	20 ± 1.0	0.96 ± 0.13	21 ± 1.0	–	8.7 ± 1.6	3.0 ± 0.2	5.7 ± 0.2	–	7.87	72
Mondego Riv 7	5.1 ± 0.2	0.23 ± 0.03	5.4 ± 0.2	1.3 ± 0.2	3.2 ± 0.2	–	8.5 ± 0.4	0.18 ± 0.07	6.61	–
Mondego Riv 8	7.2 ± 0.2	0.32 ± 0.03	7.7 ± 0.2	1.8 ± 0.2	6.1 ± 0.4	–	7.6 ± 0.3	0.27 ± 0.06	6.50	–
Suspended matter (kBq kg^{-1} ± 1σ)									mg L^{-}	
QB1-open pit	5.4 ± 0.2	0.22 ± 0.02	5.6 ± 0.2	31 ± 2	12.4 ± 1.2	36 ± 1	35 ± 2	0.047 ± 0.007	11.5	
QB2-water line	0.42 ± 0.02	0.014 ± 0.004	0.41 ± 0.02	6.7 ± 0.4	1.6 ± 0.4	0.94 ± 0.05	0.93 ± 0.04	0.011 ± 0.002	90.9	
QB3-water line	0.75 ± 0.03	0.043 ± 0.006	0.69 ± 0.03	4.4 ± 0.3	4.0 ± 0.7	1.18 ± 0.05	0.96 ± 0.04	0.005 ± 0.002	57.6	
CB1-mine water	2.2 ± 0.1	0.16 ± 0.03	2.5 ± 0.2	2.9 ± 0.2	4.6 ± 0.2	17.8 ± 0.7	36 ± 2	0.12 ± 0.02	6.0	
CB2-well	3.4 ± 0.1	0.17 ± 0.02	3.3 ± 0.1	0.11 ± 0.01	0.68 ± 0.06	5.9 ± 0.2	3.4 ± 0.1	0.025 ± 0.004	6.3	
CB3-well	3.2 ± 0.1	0.15 ± 0.02	3.2 ± 0.1	0.34 ± 0.03	2.0 ± 0.4	26 ± 1	11.2 ± 0.4	0.031 ± 0.07	2.5	
CB4-well	23.3 ± 0.7	1.02 ± 0.08	21.7 ± 0.6	2.9 ± 0.2	6.9 ± 0.7	13.4 ± 0.7	15.7 ± 0.7	0.16 ± 0.02	0.7	
Castelo Stream1	18.3 ± 0.7	0.86 ± 0.06	17.8 ± 0.7	0.53 ± 0.03	4.0 ± 0.1	2.02 ± 0.08	1.67 ± 0.09	0.064 ± 0.007	2.5	
Castelo Stream3	72.2 ± 2.6	2.9 ± 0.1	68.5 ± 2.4	0.31 ± 0.02	1.5 ± 0.1	0.84 ± 0.03	0.73 ± 0.03	0.126 ± 0.09	11.3	
Castelo Stream6	19.7 ± 0.9	0.9 ± 0.1	19.7 ± 0.9	1.3 ± 0.1	25.3 ± 2.9	–	6.6 ± 0.3	0.41 ± 0.06	0.6	
Mondego Riv 7	0.43 ± 0.01	0.019 ± 0.002	0.42 ± 0.01	0.34 ± 0.01	0.30 ± 0.02	–	0.67 ± 0.02	0.060 ± .004	14.6	
Mondego Riv 8	0.73 ± 0.02	0.035 ± 0.003	0.79 ± 0.02	0.54 ± 0.02	0.47 ± 0.02	–	1.01 ± 0.03	0.090 ± .005	10.0	

Water pH, sulfate ion concentration (mg L^{-1}) and load of suspended matter (mg L^{-1}) are also shown

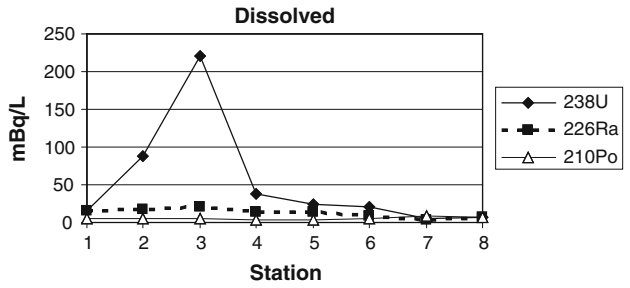

Fig. 2 Radionuclide concentrations in the dissolved phase of Castelo Stream and Mondego River waters. Location of sampling stations are indicated in Fig. 1

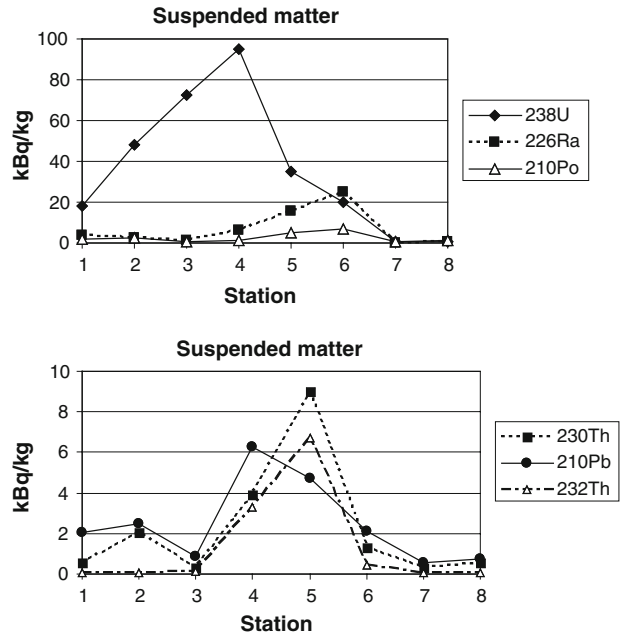

Fig. 3 Radionuclide concentrations in the particulate phase of Castelo Stream and Mondego River waters

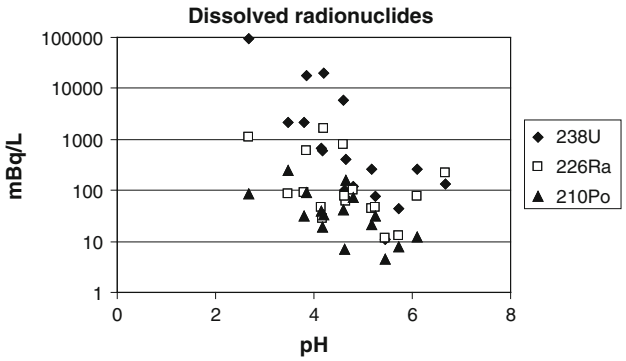

Fig. 4 Concentration of dissolved radionuclides in water from wells and uranium mines as a function of water pH. Probability of the negative correlation least-squares fit between concentration of radionuclides and water pH is $p < 0.001$ for ^{238}U, $p < 0.10$ for ^{226}Ra, and $p < 0.01$ for ^{210}Po

reaching the subsurface aquifer at about 5 m depth, frequently displayed low pH, between 4 and 5.5, and high sulfate content, usually ranging from 400 to 1,500 mg L^{-1}. These waters were analyzed for uranium series radionuclides and major ions. A significant negative correlation ($r^2 = 0.74$, $p < 0.01$) was found between sulfate ion concentration and pH in mine waters and well waters (not shown). Concentrations of dissolved uranium series radionuclides decreased with increasing pH values (Fig. 4), i.e., radionuclide concentrations were higher in waters with higher sulfate ion concentrations. Incidentally, this result suggests the use of a simple method, based on the measurement of acidity or dissolved sulfate with a portable probe, to monitor the spread of radioactive contamination in ground waters of this area.

Low pH and high radioactivity in well waters, sometimes even higher than in the effluents discharged into the creek, suggest that the past use of sulfuric acid for in situ uranium leaching in the underground mine of Cunha Baixa originated the acid waters that circulate today in the fractured rock and infiltrated the subsurface aquifer. The circulation of groundwater from Cunha Baixa mine reaches the low lands on the east bank of Castelo Stream and likely caused the enhanced radionuclide concentrations in most of the wells in this area (Table 1).

Previous work carried out in this area had determined high ^{226}Ra concentrations also in water from wells. These high ^{226}Ra concentrations were considered as originating in mine waste water releases as well as in radium leaching from tailing piles disposed near the mine (Pereira et al. 2005). Geochemical investigations in the area had found enhanced concentrations of uranium in soils and stream sediments due to the dispersal of uranium with waste waters originated in both mines (Santos Oliveira et al. 2005). Furthermore, a preliminary assessment of the chemical impact resulting from the operation of Cunha Baixa mine mainly focused on sulfate, Al, Mn and U concluded that mine water releases affected surface and groundwater quality in a range of about 1.5 km downward from the mining site (Neves et al. 2005).

Irrigation with these well waters was considered likely to increase concentrations of stable metals and radionuclides in soils and, thus, could expose consumers to the intake of stable metals and radionuclides higher than background values in the region (Neves et al. 2005). Further work should elucidate the transfer of radionuclides to plants grown in this agriculture area.

Results of this survey showed that concentrations of uranium series radionuclides in acid waters from the underground Cunha Baixa mine and from the open pit of Quinta do Bispo mine are very high. The treatment of these acid waters with calcium hydroxide, followed by sludge decantation in ponds, removes a large fraction of

radioactivity in water discharges, although concentrations of radionuclides in water and suspended matter of the Castelo Stream still showed enhanced radioactivity values due to mine effluent discharges. Nevertheless, enhanced radionuclide concentrations did not spread very far from mine sources and radionuclide concentrations in the river were already near background values before reaching the artificial lake in Mondego River.

Surface waters are not the only water body receiving acid mine waters and treated mine effluents from these uranium mines. In the agriculture area of Cunha Baixa, irrigation wells showed a trend in sulfate ion concentrations and pH values that pointed out to Cunha Baixa mine water as the source for ground water contamination. Well waters displayed high radionuclide concentrations associated to high sulfate concentration and low pH values, thus confirming the contamination of the aquifer by acid mine water.

Radioactivity in wells water is higher than EU water quality guidelines for human consumption, i.e., 0.5 and 1.0 Bq L^{-1} for total alpha and total beta activity, respectively. Regular consumption of these waters could expose members of the public to radiation doses above 0.1 mSv $year^{-1}$, and the use of this water as drinking water should be banned. Irrigation of horticulture plots with water from these wells is likely to gradually increase radioactivity in the soil top layer and could be transferred to vegetables and grains. This way, radionuclides may be transferred throughout the food chain to cattle and to man. The radiological risk of this potential contamination pathway to man would be assessed in future work. Moreover, environmental remediation of this area should be planned to prevent further leaching of mining and milling tailings, and to reduce contamination of the aquifer as well as to protect surface waters from contamination with mine effluent discharges.

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