

## Spatial variability of soils and stream sediments and the remediation effects in a Portuguese uranium mine area



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### ABSTRACT

The old Senhora das Fontes uranium mine, located in central Portugal, was closed down in 1971. The treatment of ores from this mine and other mines by heap-leach ended in 1982. Seven dumps partially covered by vegetation were left in the area. Soil and stream sediment samples were collected in December 2009. The remediation was carried out from May 2010 to January 2011. Stream sediment samples were collected again in October 2013. Before the remediation, soils from inside the mine influence area have higher Al, As, Co, Cr, Cu, Fe, Ni, Sr, Th, U and Zn concentrations than soils from outside this area, due to radionuclides, metals and metalloid released from the mine dumps. The principal component analysis (PCA) shows a distinction between soils from inside and outside the mine influence area. The U(VI), As(V) and metals from soils can be adsorbed to Fe-oxyhydroxides and the humic acid can increase the U uptake. Soils must not be used for public or private green and residential areas, because they are contaminated in U, As, Co, Cd and Ni. Before the remediation, downstream sediments have higher Al, As, Cu, Mn, Ni, Pb, U and Zn than upstream sediments, due to erosion and percolation of water through the mine dumps. The PCA shows a distinction between downstream and upstream sediments. The U(VI), Th and As(V) can be adsorbed to Fe-oxyhydroxides. The stream sediments are contaminated in As, Mn, Th and U. Downstream sediments are the most contaminated in U and As. After the remediation, upstream and downstream sediments have generally higher Al, Fe, As, Cr, Ni, Th, U and Zn concentrations than before the remediation, attributed to the relocation of dumps. Radionuclides, metals and metalloids were transported by surface water. Consequently downstream sediments have higher Al, As, Cu, Mn, Ni, Th, U and Zn concentrations than upstream sediments. The U(VI), Th and As(V) can be adsorbed to Fe-oxyhydroxides. Stream sediments became more contaminated in U, Th and As than before the remediation, but more intensively downstream.

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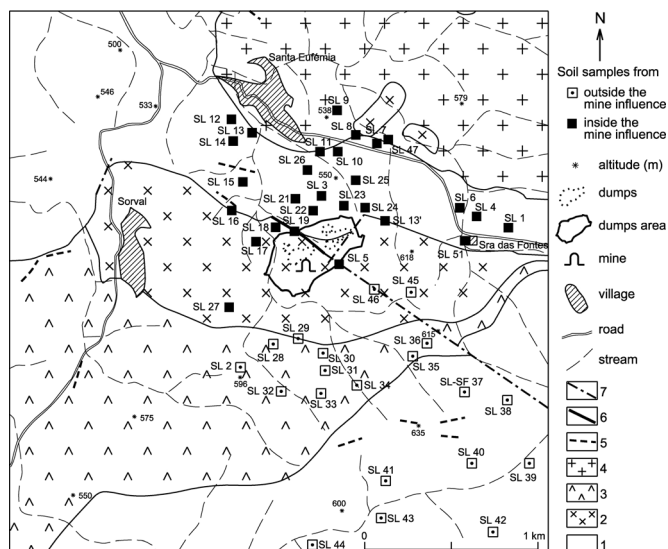
### 1. Introduction

The effects of old mines and the release of mine drainage after their abandonments will promote different effects to the health and environment. Uranium is a potential environmental pollutant. Moderate to high concentrations of U, such as in some old mine

areas, can be harmful to plants, wildlife and human populations due to prolonged exposure (e.g. Craft et al., 2004). The extent of contamination is not limited to the vicinity of mines, as contaminated material may be physically remobilized, particularly in high flow conditions, causing dispersion of pollutants over hundreds of kilometers from historical mining sites (e.g. Grosbois et al., 2012). Portugal has about 58 uranium deposits, which were abandoned (Pinto and Silva, 2005). In some of them, uranium ore was crushed, milled and leached with H<sub>2</sub>SO<sub>4</sub> to obtain uranium from the ore. In the mine sites, there are tailings, heap-leach residues and contaminated waste rocks accumulated in dumps. The erosion and

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**Fig. 1.** Geological map containing the Senhora das Fontes old uranium mine, dumps, streams and locations of soil samples (SL). 1 – schist-greywacke complex; 2 – Senhora das Fontes-Sorval orthogneiss; 3 – Póvoa d’el Rei orthogneiss; 4 – Santa Eufémia granite; 5 – quartz vein; 6 – basic rock vein; 7 – fault.

weathering of dumps causes contamination of groundwater and surface water (e.g. Pinto et al., 2004; Gómez et al., 2006; Neiva et al., 2014, 2015). Metals and metalloids are retained in organic matter (e.g. Schaller et al., 2011) and inorganic phases (e.g. Mulligan et al., 2001) from stream sediments and soils, which become contaminated (e.g. Lottermoser and Ashley, 2006; Lottermoser et al., 2005; Neiva et al., 2014).

The remediation of some uranium mines has been carried out with some success in Western Europe, at Wismut in Germany and Limousin district in France and also in North America, at Elliot Lake in Canada and UMTRA programme in USA, over the past twenty years (Waggit, 2008). However, there are many examples of poor or no remediation that remain as a legacy from former times, due to the lack of legislation in earlier times and because remediation of former uranium mines is very expensive (Waggit, 2008).

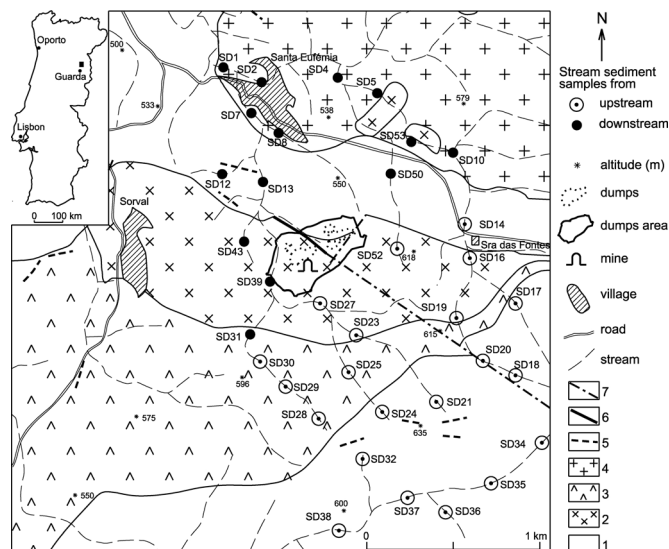
This paper presents the study of the environmental risks associated with the Senhora das Fontes abandoned uranium mine area (Portugal) on soils and stream sediments before the remediation and stream sediments after the remediation. The results allow assessing the impacts of the remediation process in stream sediments and consequently suggest the improvement of the remediation and techniques to avoid similar negative results in other mine areas.

## 2. Mineralization and methods

### 2.1. The mine site

The old Senhora das Fontes uranium mine is located in the Guarda district, central Portugal. It is close to Sorval and Santa Eufémia villages (Figs. 1 and 2). Two orthogneisses and a granite intruded the schist-greywacke complex (Beira group). They are mainly cut by basic rocks and quartz veins (Macedo, 1988).

The mine consists of divided quartz veins that penetrated fractured shear zones at the contact of the schist-greywacke complex (locally consisting of graphite schists) with the Senhora das Fontes-Sorval orthogneiss. They contain tourmaline, cassiterite and autinite down to a depth of 40 m. Located below, cutting the schists, there are small veinlets and elongated nodules which contain black uranium oxides, uraninite and Fe-saleeite. The uranium mineralization is supported by the graphite schists, which are



**Fig. 2.** The same geological map of Fig. 1 with the locations of stream sediment samples (SD).

also cut by basic rock veins where secondary uranium minerals are trapped. The Senhora das Fontes uranium deposit contains a mean of 0.4%  $U_3O_8$ , but reaching to 1–2%  $U_3O_8$  (Barros, 1966). It was exploited underground in three levels down to a depth of 900 m. The mine was closed down in 1971. Afterwards, the  $190 \times 10$  m lense-shaped upper mineralized massif was removed (Barros, 1966), and a small open pit was made where U was removed by the heap-leach process (to add sulphuric acid to crushed ore to dissolve it and oxidize U) being the U enriched solution collected inside the mine until 1982. Uranium ores from other mines were also treated in the area by heap-leach static threshing floors. Seven dumps, partially covered by vegetation, were left in the area.

At the old Senhora das Fontes uranium mine area, located in central Portugal, the total volume of contaminated materials and soils was about  $73641 \text{ m}^3$ . The remediation plan consisted of different works (EDM Report, 2008). The main well of 90 m depth, connected to the three mine levels and other openings to the underground mine were closed with concrete. The open pit was covered with a minimum of 2 m of soil, being 1 m of new soil and the other meter composed of selected soils. A temporary drainage system, surrounding the most contaminated areas, was built with concrete to avoid their contacts with rainwater. The collected drainage water was gathered in a decantation lake of 20000 L capacity provided with a geomembrane and located at NE of the mine area. Calcium hydroxide,  $Ca(OH)_2$ , was added to the water to get a minimum pH value of 9. The precipitation of suspended solid material was promoted by the addition of a flocculant. The muds were dried and located in an impermeable cavity. The uncontaminated rainwaters, after having been treated, were sent to the stream.

A temporary deposit was prepared to store the materials from the demolition of buildings made of bricks and concrete and materials accumulated in seven dumps ( $27000 \text{ m}^3$ ), that were left in the area and partially covered by vegetation. Two of the dumps contained decantation muds and waste materials of larger grain-sizes and another one with dissolved waste precipitates. A fourth one consisted of waste materials from the open pit and three others with ore dissolution wastes from the open pit. Contaminated soils were also carried to the temporary deposit.

The decantation lake for rainwater with a capacity of 10000 L was displaced towards SW, mainly to collect the waters that percolated the materials accumulated in the temporary deposit. A similar

**Table 1**

The results in mg/kg of the validation procedure using the certified sewage sludge amended soil BCR-143R.

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Obtained mean values	71.5 ± 1.5	10.4 ± 0.3	424 ± 2	126 ± 2	858 ± 2	295 ± 3	174 ± 1	1061 ± 2
N	12	8	12	12	12	12	12	12
Certified mean values	72.0 ± 1.8	11.8 ± 1.0	426 ± 12	128 ± 7	858 ± 11	296 ± 4	174 ± 5	1063 ± 16
N	6	8	8	8	8	6	8	9

N—number of replicates. Certified values are not available for Al, Fe, As, Sb, Sr, Th and U of the BCR-143R.

treatment to what it was done at the NE of the mine was applied to the water collected in this lake. A total of three independent and impermeable cavities, separated by soil materials, with basal drainage systems were built in the same place where dumps were before to store the dried muds, and all the materials from the temporary deposit. They were sealed, covered with erosion resisting covers and a surface drainage system was installed. The topography of the area was reorganized. The remediation was carried out from May 2010 to January of 2011.

The local stream sediments contain clasts of weathered schists, metagreywackes, orthogneisses, granite and quartz veins. The area has humic cambisol (Food and Agriculture Organization of the United Nations, 2014) and is mainly covered by oaks, pinus and underbrush, but downstream there are also rye fields and pastures. There are also many different types of crops in the fields during the spring.

## 2.2. Analytical methods

A total of 48 soil samples were collected in an area of about 4 km<sup>2</sup> (Fig. 1), which include 28 soil samples from inside the area that receives the mine influence and 20 soil samples from an adjacent area outside the mine influence, in order to represent a natural background. They were collected in October 2009. A total of 34 samples of stream sediments were collected, 21 upstream and 13 downstream from the old Senhora das Fontes uranium mine area in December 2009, before the remediation. Later in October 2013, after the remediation, 13 upstream sediment samples and 13 downstream sediment samples were collected from selected spots used before the remediation (Fig. 2). The soil and stream sediment samples were collected at a depth between 20 and 30 cm. They were transported to the laboratory 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 (British standard, 1995a). The electrical conductivity (EC) was measured in a liquid/solid ratio of 1/5 (British standard, 1995b). Only the < 250 μm fraction of soil and stream sediment samples were digested with *aqua regia* (3:1 HCl-HNO<sub>3</sub>), filtered through a 2 μm filter and analyzed by an ICP-OES using a Horiba Jobin Yvon JY 2000 2 spectrometer with a monochromator to determine metals and metalloids. An internal reference soil, prepared with *aqua regia* and validated using the certified sewage sludge amended soil BCR-143R, was used (Table 1). Duplicate blanks and a laboratory standard were included in each batch of 26 samples. Detection limits (DL) were estimated on instrumental basis using internal standard routines. According to the ICP-OES (User manual, 2001), detection limits were accessed using blanc signal and dispersion estimated by sampling signal in the 0.5 s interval. The conversions from mg/L to mg/kg were estimated using the following equation  $DL(\text{mg/kg}) = (X \cdot 0.1) / m$ , where X is the DL at (mg/L) given by the ICP-OES and m is the average of the heavy masses of the samples in kg. The detection limits in mg/kg for soils and stream sediments are 1.93 for Al, 1.40 for Fe, 3.0 for As and Sb, 0.60 for Cd, 2.4 for Co, Cu, Mn and Pb, 0.67 for Cr, 2.6 for Ni, 1.80 for Sr, 3.4 for Th, 0.80 for U and 0.61 for Zn. The precision is up to 6%.

These determinations were carried out at the Department of Earth Sciences, University of Coimbra, Portugal.

Cation exchange capacity (CEC) and organic matter (OM) were determined in 30 representative soil samples, 29 stream sediment samples collected before the remediation, and 22 stream sediment samples collected after the remediation in spots with the highest U and Th concentrations. These determinations were carried out at the Department of Biology and Environment, University of Trás-os-Montes and Alto Douro, Portugal. The CEC was obtained as the sum of extractable bases and extractable acidity by the ammonium acetate solution (pH7), according to the method of Thomas (1982) with a precision of 3%. The organic carbon content was determined using an Primac SCN, Skalar elemental analyser. CO<sub>2</sub> was quantified by an NIRD (near infrared detector), after oxidation at 1100 °C, and CO<sub>2</sub> 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 obtained was 3% for soil and stream sediment.

The grain size distribution and textural characteristics were obtained in 12 soil and 29 stream sediment representative samples collected before the remediation and 22 stream sediment samples collected after the remediation at the Department of Earth Sciences, University of Coimbra, Portugal. These samples were selected due to their highest U and Th contents, so that it could be understood if the concentrations of these radionuclides are related to the grain size. 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; precision up to 5%). X-ray diffraction, using a Philips PW3710 X-ray diffractometer, with a Cu tube, at 40 kV and 20 nA, was applied for the mineralogical identifications of clay minerals in the <2 μm fraction in oriented samples before and after treatments with ethylene glycol and heating up to 550 °C.

The principal component analysis (PCA) was applied to 48 soil samples data and 30 stream sediment samples data collected before the remediation. Four principal components were extracted from each data set following the Kaiser's criterion (Kaiser, 1960), and those principal components with eigenvalues > 1 were retained for further interpretation.

A descriptive statistical study has been developed with the 13 upstream sediment samples and 13 downstream sediment samples concentrations from before the remediation. The Spearman coefficient (r) for a 1% significance level (0.01) was calculated as a measure of the correlation between variables (As, Fe, U and Th). The presented statistical results were obtained with the statistical tool box of Matlab software 2010. A similar descriptive statistical study was done for 13 upstream sediment samples and 13 downstream sediment samples after the remediation.

## 3. Results and discussion

### 3.1. Geochemistry of soils before the remediation

The textural and mineralogical characteristics, physical-chemical parameters and concentrations of metals and metalloids of soils from the Senhora das Fontes old uranium mine area are given in Appendices A, B. The grain size distribution of the studied

soil samples (<2 mm) comprises 46.7–91.3% of sand (2 mm–63  $\mu\text{m}$ ), 7.6–49.5% of silt (63–4  $\mu\text{m}$ ) and 0.74–3.8% of clay (<4  $\mu\text{m}$ ). They consist of quartz about (9–100%), muscovite/illite (up to 88%), K-feldspar (up to 21%) and albite (up to 20%) (Appendix A). The clay minerals are illite (6–74%), kaolinite (17–71%), vermiculite (up to 28%), even though vermiculite only occurs in five samples, montmorillonite was only found in one sample and is 77% and chlorite is 10% only in one sample. Novacekite  $\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_{10}$  or  $12\text{H}_2\text{O}$  and vanuranylite  $(\text{H}_3\text{O}, \text{Pb}, \text{K}, \text{Ca})_2(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$  were also found, by XRD, in most samples. There are no significant differences in the textural characteristics between samples collected from outside and inside the mine influence area. The content of each clay mineral though is up to a higher value inside than outside the old mine area and dumps influence.

In general, soils from inside the mine influence area have higher OM contents (up to 7.3%) than those from outside this area that are unaffected by the dumps (Appendix B), which can be attributed to the agricultural activities downstream of this abandoned mine. The cation exchange capacity is low and mainly between 0.33 and 8.0 cmol/kg, without a good distinction relatively to the mine influence, but the highest value, of 20.5 cmol/kg, occurs in a soil sample from inside the mine influence area, indicating higher metal and metalloid contents. The pH values range from 4.1 to 6.9, showing that they are acid to neutral, due to the influence of mine tailings, orthogneisses and granite. The EC values are low, ranging from 8 to 155  $\mu\text{S}/\text{cm}$ , suggesting a low contamination. The highest value occurs within the old mine influence area (Appendix B).

In general, Al, As, Co, Cr, Cu, Fe, Ni, Sr, Th, U and Zn concentrations are higher in soil samples from inside the mine influence area than those in soil samples collected from the outside (Appendix B, Fig. 3) and the highest EC and CEC values of 155  $\mu\text{S}/\text{cm}$  and 20.5 cmol/kg, respectively, occur in soil samples from inside the mine influence area. The metals and metalloids are released from the mine dumps and consequently may be more concentrated in soils closer to the mine. The adsorption of metals in soils increases in near neutral to alkaline pH (Alloway, 1995). Adsorption of U by Fe-oxides is extensive in the absence of dissolved carbonate, but decreases when carbonate and organic matter are present. Uranium at acid conditions is present as  $\text{UO}_2^{2+}$ , under neutral conditions occurs as hydroxide complexes, and its adsorption increases with the increase of the CEC. In the soils from the Senhora das Fontes uranium mine area, uranium increases in samples with high CEC (Appendix B). The adsorption of arsenic, in the form of arsenate As(V), increases until pH5 for clays, but its adsorption by Fe oxides decreases above pH7 (Goldberg, 2002). Therefore, arsenic retentions in soils from the Senhora das Fontes area tend to be higher in samples with pH higher than 5 (Appendix B).

The principal component analysis (PCA) was applied to the measured physical-chemical parameters and analyzed metals and metalloids from 48 soil samples (Table 2). Organic matter, cation exchange capacity, temperature, Cd and Sb were not included because spatial variability was not explained. The three components explain most of the data variability (78% of the total variance), with a variance of approximately 64.9% in PC1, 7.4% in PC2, 6.0% in PC3. Most metals Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Th, U and Zn and the metalloid As are correlated and define an association with positive loading in the PC1 (Table 2, Fig. 4a). In general, the PCA shows a distinction between soil samples from outside and inside the mine influence area, because most elements Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Th and Zn are plotted in the positive side of PC1 coincident with most soil samples collected inside the mine influence area (Fig. 4b). The EC and pH are mainly explained by PC2 and PC3, respectively, suggesting that they are not the principal parameters that control the mobility of metals, As and radionuclides in the soils from outside the mine influence area (Table 2), because metals, As and radionuclides are probably mainly retained in oxyhydroxides.

**Table 2**

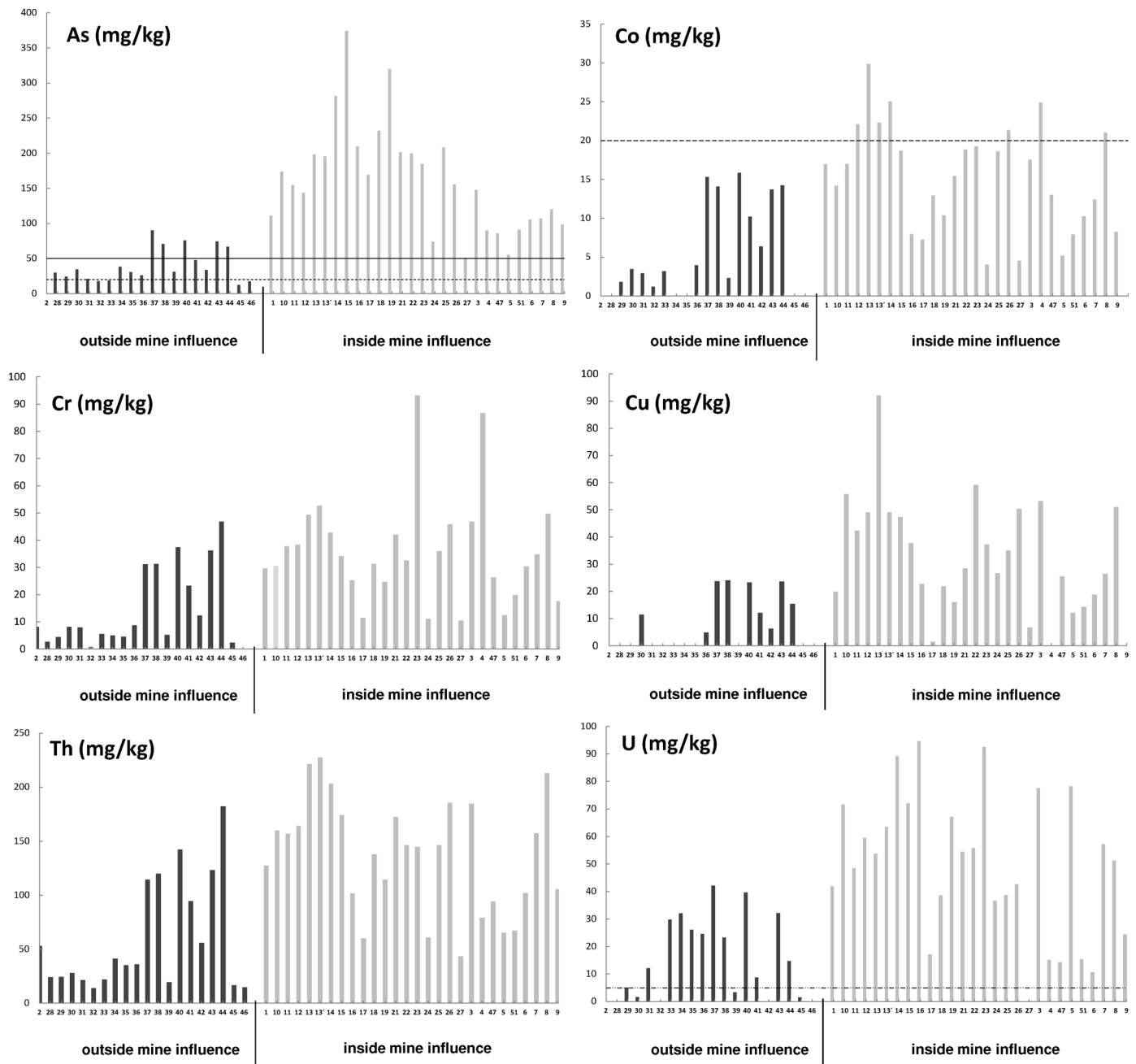
Principal component analysis of soils, before the remediation, from the Senhora das Fontes old uranium mine area.

	PC 1	PC 2	PC 3
Al	<b>0.784</b>	−0.305	−0.041
As	<b>0.778</b>	−0.150	−0.181
Co	<b>0.916</b>	−0.048	−0.147
Cr	<b>0.777</b>	0.010	−0.413
Cu	<b>0.885</b>	−0.184	0.201
Fe	<b>0.945</b>	−0.117	0.116
Mn	<b>0.711</b>	0.299	0.196
Ni	<b>0.882</b>	0.001	−0.057
Pb	<b>0.773</b>	0.163	0.162
Sr	<b>0.813</b>	0.231	−0.188
Th	<b>0.943</b>	−0.181	0.026
U	<b>0.756</b>	−0.237	−0.137
Zn	<b>0.951</b>	0.101	0.108
pH	0.523	0.138	<b>0.663</b>
EC	0.470	<b>0.804</b>	−0.196

Loading values for the PC axis higher than +0.5 and lower than −0.5 are given in bold.

The study area belongs to the Beira granitic batholith, which contains uranium minerals (Cotelo Neiva, 2003) and is an important source of uranium (Porcelli et al., 1997). The Senhora das Fontes-Sorval orthogneiss (Fig. 1) contains torbernite and saleeite (Macedo, 1988). Therefore, the composition of the soils was influenced by the granitic country rocks, the quartz veins containing autunite, black uranium oxides, uraninite and Fe-saleeite that compose the old Senhora das Fontes uranium mine, and also the tailings.

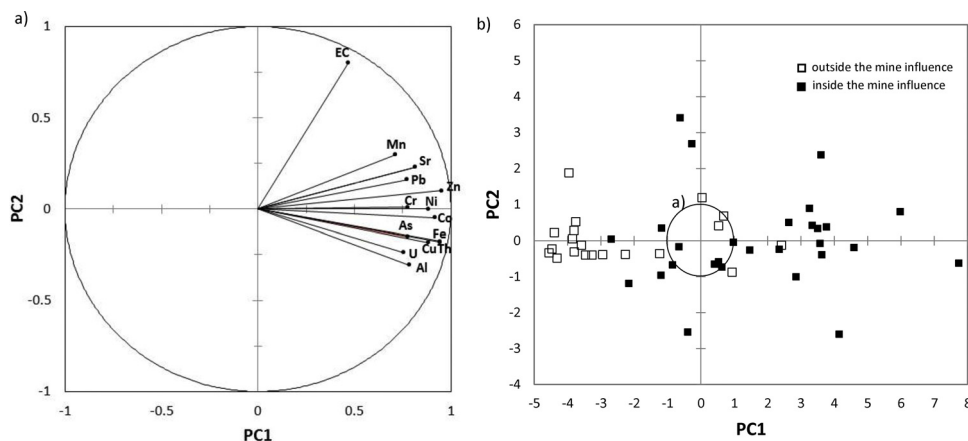
Uranium in soils is largely controlled by the composition of the groundwater containing natural and contaminant U(VI) complexing ligands such as sulfate, carbonate and phosphate, and organic chelators (e.g. Langmuir, 1978). In the Senhora das Fontes mine area, uranium from groundwater was mainly transported as U(VI) by soluble carbonates, as indicated by the speciation modelling (Neiva et al., 2015). The software Phreeq C and the minteq.V 4.dat database were used for modelling metals and arsenic, whereas the sid.dat database was used for uranium modelling. The alkaline earth element reactions and log k values were added to the Phreeq C input file for uranium modelling (according to Dong and Brooks, 2006; Geipel et al., 2008). The surface of soil at pH < 5 has a positive charge that would attract anionic species (e.g. Sparks, 2003). The most important inorganic adsorbent phases for U(VI) are goethite and ferrihydrite due to their ubiquity in waters and sediments and their high surface areas (e.g. Bruno et al., 1995; Gabriel et al., 1998). The precipitation of goethite in groundwaters, but in surface waters seems to be evident due to the high saturation indices obtained by geochemical modelling (Neiva et al., 2015). Therefore, the soils inside the old mine influence area contain up to 48.1 g/kg Fe (Appendix B) which is the highest concentration from these soils, suggesting that the Fe-oxyhydroxides were important adsorbent phases, retaining radionuclides, metals and metalloids in soils from this area as in another Portuguese uranium mine area (Neiva et al., 2016). As the studied soils have pH < 7 (Appendix B), the humic acid increases the U uptake (Payne et al., 1996). Uranium is mobilized at high pH, which is the opposite of most metals, due to the formation of soluble carbonate complexes. The slightly acid to neutral pH conditions in soils from the Senhora das Fontes uranium mine area (Appendix B) favor the uranium fixation on solids (Langmuir, 1978; Duff and Amrhein, 1996). Organic carbon is a major uranium binding partner in soils (e.g. Gruan et al., 2000). Reductive precipitation of uranium minerals is considered a major and sustainable mechanism, because uranium (IV) minerals are rarely soluble under reducing conditions (Schöner et al., 2009; Cabral Pinto et al., 2008, 2009). However, initial fixation may be due to adsorption rather than reductive precipitation (Zielinski et al., 1987).



**Fig. 3.** Selected concentrations of some metals and metalloid of soils from the Senhora das Fontes old uranium mine area. Maximum levels for --- public, private green areas and residential sites; — industrial areas (Decreto Ministeriale, 1999).

The concentration of As is high up to 375 (mg/kg) in soils from inside the Senhora das Fontes uranium mine influence area (Appendix B). The arsenic has a low mobility in soils and is mainly retained in oxyhydroxides (García-Sánchez et al., 2010), particularly in the Fe-oxide soil fraction close to old mining activities from different countries (Gál et al., 2006) and in Fe-oxyhydroxides (goethite, hematite and ferrihydrite) from some Portuguese As-Au and Sb-Au mineralized areas (Carvalho et al., 2012). The soils of the Senhora das Fontes mine area contain up to 48.1 g/kg Fe (Appendix B), suggesting that As is adsorbed by Fe-oxyhydroxides. The pH of the studied soils is of 4.1–6.9 (Appendix B) and arsenic was transported mainly as  $\text{H}_2\text{AsO}_4^-$  in groundwater with pH values of 4.2–7.3 (Neiva et al., 2015). Therefore, the As(V) will be more easily adsorbed to goethite and amorphous iron oxide than As(III) at a pH lower than 5–6, since the trivalent As is more easily

adsorbed by those solids at a pH higher than 7–8 (Dixit and Hering, 2003). The PC1 association (Fig. 4a) suggests that Fe-oxyhydroxides retain metals, metalloid and radionuclides affecting their mobility. The highest organic matter value of 7.3% (Appendix B) occurs in a soil sample from inside the mine influence area reflecting a higher retention of heavy metals in soils from the mine influence area than in those from outside the mine influence area. Organic matter retains heavy metals in soils, forming insoluble and soluble complexes with them (Kabata-Pendias and Mukherjee, 2009). As the soils have a low clay size fraction (less than 3.8%), comprising the clay minerals kaolinite, illite, vermiculite and montmorillonite (Appendix A), they cannot retain significant concentrations of metals and metalloids. But among them, montmorillonite can be the best mineral for the retention due to its structure.



**Fig. 4.** Plot of PC1 and PC2 planes from soils of the Senhora das Fontes old uranium mine area (a); plot of variable weights of soils in principal components identified by Principal Component Analysis (b).

**Table 3**

Comparison of metal and metalloid contents (mg/kg), except Fe (%), obtained by *aqua regia* digestion of soils, before the remediation, from the Senhora das Fontes old uranium mine area with those of another Portuguese uranium mine area.

	S. Fontes: before the remediation			Pinhal do Souto (1)		
	Median	Maximum	N	Median	Maximum	N
As	90.1	374	48	94.9	19.6	47
Co	11.4	29.9	48	0	52.9	47
Cr	28.0	86.7	48	1.22	17.3	47
Cu	19.3	92.1	48	10.4	237	47
Fe	2.20	4.8	48	8.7	15.1	47
Mn	553	2080	48	214	60.1	47
Ni	22.6	119	48	0	46.1	47
Pb	22.5	48.8	48	62.2	944	47
Th	104	228	48	26.2	47.2	47
U	32.1	94.6	48	25.1	337	47
Zn	69.0	160	48	92.7	347	47

(1) Neiva et al. (2014); N-number of determinations.

### 3.2. Contamination in soils before the remediation

The contamination of soils from the Senhora das Fontes uranium mine area can be defined by comparing the total element concentration with the maximum accepted soil levels according to the Italian Legislation (Decreto Ministeriale, 1999). The levels of soil contamination accepted for land usage for industrial purposes is higher than for the usage as public, private green areas and residential sites. But this legislation does not provide values for some metals such as U. The soils from the study area are contaminated in As and forbidden for public or private green and residential areas and the soils located inside the mine influence area should not be even used for industrial occupation (Fig. 3). Some soils are contaminated in Co, Cd and Ni and consequently must not be used for public or private green and residential areas (Fig. 3). In soil samples from inside the old mine influence area, the U concentration reaches 94.6 mg/kg and in several soil samples from outside this area, its U concentration is higher than 5 mg/kg (Appendix B), that is the value beyond which soils are considered contaminated in U (Ribera et al., 1996).

The median concentrations of Co, Cr, Cu, Mn, Ni, Th and U of soils from this area are higher than those of the abandoned Pinhal do Souto uranium mine area (Neiva et al., 2014) (Table 3). The processes of U removal from ores of the Senhora das Fontes mine and other close U mines that took place at the Senhora das Fontes mine area had an important influence in the higher degree of contamination in U, metals and metalloid of soils from this area than in the Pinhal do Souto area. Therefore, soils from Senhora das Fontes area

are contaminated mainly due to the combination of two important factors: the presence of dumps, and the local performance of U removal processes on the ores extracted from this mine and from other nearby deposits. The observed high levels of U, metals and As of these soils cause an impact on cultivated soils located immediately downstream of mine dumps and spread more than 1 km away from the mine dumps, dangerously close to the Santa Eufémia village. The main effects on cultivated soils may be the accumulation of metals and As in crops and reduced plant growth (e.g. Sheppard, 1992).

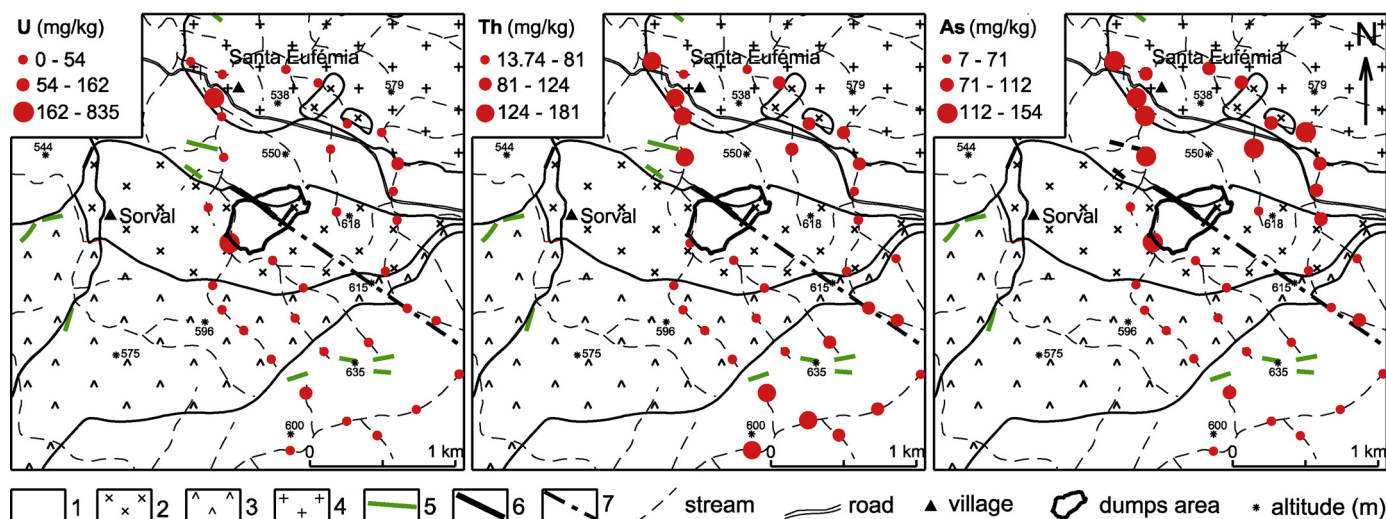
### 3.3. Geochemistry of stream sediments before the remediation

The textural characteristics, physical-chemical parameters and concentrations of metals and metalloids in stream sediments before the remediation from the Senhora das Fontes mine area are given in Appendices C and D. These stream sediments contain mainly sand (2 mm–63 μm) and silt (63–4 μm) fractions, and a minor clay size (< 4 μm) fraction up to 3.0%. The < 2 μm clay size fraction contains 43–63% of illite, 24–29% of kaolinite and up to 24% of vermiculite, 10% of chlorite and 2% of montmorillonite. Illite and kaolinite reach higher amounts in sediments downstream from the mine and dumps, but vermiculite reaches a higher amount on an upstream sediment sample.

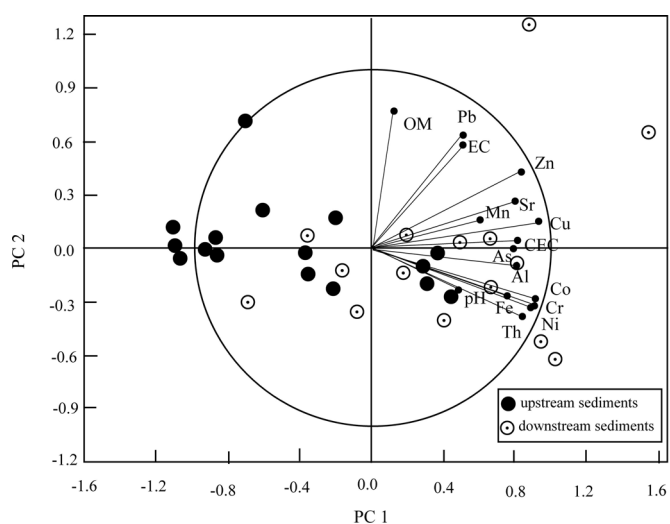
The pH values in upstream and downstream sediments are of 4.3–5.7 and 4.3–6.6, respectively (Appendices C, D). The electrical conductivity (EC) ranges from 13 to 55 μS/cm in upstream sediments and from 13 to 168 μS/cm, and with only a value of 534 μS/cm in downstream sediments, indicating that generally the contamination is low. The CEC is of 0.39–5.6 cmol/kg in upstream sediments and of 0.76–5.8 cmol/kg in downstream sediments. The OM values are of 0.40–4.7% in upstream sediments and 0.28–8.6% in downstream sediments.

The main stream that drains the mine dumps had, before the remediation, stream sediments with the highest U (834 mg/kg) and As (153 mg/kg) concentrations (Fig. 5), because they received the highest influence of the mine dumps.

In general, before the remediation, Al, As, Cu, Mn, Ni, Pb, U and Zn have higher concentrations in downstream sediments than in upstream sediments (Appendices C, D, Fig. 5), due to the erosion and leaching of the mine dumps and removing processes of uranium from ore. The PCA also shows a good distinction between downstream and upstream sediments before the remediation (Fig. 6), as downstream sediments are associated with the positive side of PC1, represented by the metals Al, Co, Cr, Cu, Fe, Mn, Ni, Sr, Th and Zn, the metalloid As and also CEC. Some upstream samples (SD18, SD



**Fig. 5.** Distribution of U, Th and As concentrations in stream sediments, before the remediation, from the Senhora das Fontes old uranium mine area. The class limits of spatial distributions are median, and median plus one, two and three standard deviations.



**Fig. 6.** Plot of variable weights of stream sediments from the Senhora das Fontes old uranium mine area, before the remediation, identified by Principal Component Analysis. All four components account approximately for 82% of the variability in the original data set with variance approximately 49% in PC1, 13.5% in PC2, 12.5% in PC3 and 8.0% in PC4.

24, SD 32 and SD38) are also plotted with them, but they do not show strong loads. Lead, EC and OM are associated with the positive loading in the PC2 (Table 4), suggesting that Pb is adsorbed into OM. Uranium has a strong negative load with the PC3 (Table 4), but only one stream sediment SD 39 is associated with this axis (Fig. 6). The pH is associated with the positive loading in the PC3.

The correlations Th-U, Fe-U, Fe-Th, U-As, Th-As and Fe-As from upstream and downstream sediments, before de remediation (Fig. 7), suggest that U, Th and As were adsorbed to Fe-oxyhydroxides (e.g. Frau and Arda, 2004; Pinto et al., 2004; Grosbois et al., 2007; Cabral Pinto et al., 2008, 2009; Carvalho et al., 2012). Iron oxyhydroxides are the main mineral phase binding arsenic (Manning and Goldberg, 1997; Larios et al., 2012). In the Senhora das Fontes mine area, uranium from surface water was mainly transported as U(VI) by soluble carbonates and adsorbed to goethite, as indicated by the speciation modelling (Neiva et al., 2015). Most of the clay minerals (illite, kaolinite, vermiculite, chlorite and montmorillonite) that occur in the studied stream sediments have a low adsorption capacity, with the exception

**Table 4**

Principal component analysis of stream sediments, before the remediation, from the Senhora das Fontes old uranium mine area.

	PC 1	PC 2	PC 3	PC 4
Al	<b>0.807</b>	-0.092	-0.247	-0.079
As	<b>0.785</b>	-0.003	-0.466	0.307
Co	<b>0.911</b>	-0.286	-0.029	-0.139
Cr	<b>0.892</b>	-0.331	-0.170	-0.047
Cu	<b>0.931</b>	0.149	0.112	0.082
Fe	<b>0.754</b>	-0.269	0.042	-0.231
Mn	<b>0.603</b>	0.158	0.219	-0.087
Ni	<b>0.902</b>	-0.321	-0.057	-0.193
Pb	0.510	<b>0.633</b>	0.279	0.351
Sr	<b>0.804</b>	0.255	0.296	0.077
Th	<b>0.843</b>	-0.372	-0.268	0.057
U	-0.007	0.020	<b>-0.679</b>	0.660
Zn	<b>0.831</b>	0.432	0.267	0.097
pH	0.488	-0.230	<b>0.583</b>	0.487
EC	0.513	<b>0.580</b>	-0.224	-0.365
CEC	<b>0.816</b>	0.039	0.043	-0.094
OM	0.132	<b>0.766</b>	-0.441	-0.173

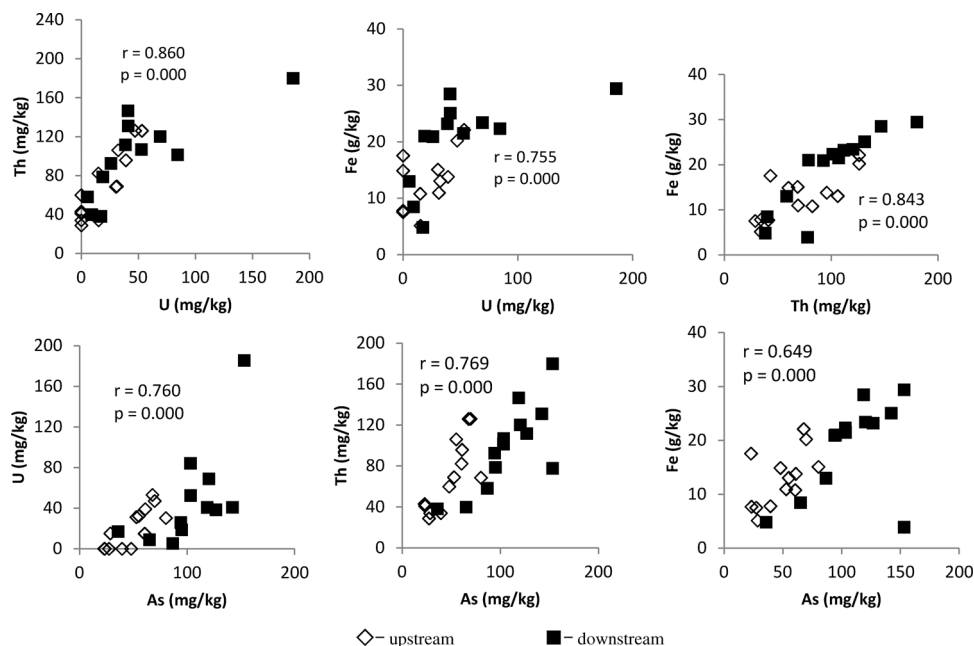
Loading values for the PC axis higher than +0.5 and lower than -0.5 are given in bold.

of montmorillonite. The montmorillonite is the clay mineral that adsorbs uranium (Catalano and Brown, 2005). The organic matter of these stream sediments is up to 8.6% and may retain some metals, As and uranium contents. Algae could have been incorporated in stream sediments as organic matter. Algae can promote reducing conditions of U(VI) to U(IV) (Duff et al., 1997). The U(IV) was certainly readily oxidized in contact with air (Duff et al., 1999). Uranium of the studied stream sediments occurs as U(VI) probably mainly adsorbed to Fe-oxyhydroxides.

The pH of the studied stream sediments ranges between 4.3 and 6.6 (Appendices C, D) and arsenic was mainly transported as  $\text{H}_2\text{AsO}_4^-$  in surface water with a pH of 5.5–7.9 (Neiva et al., 2015), suggesting that arsenic occurs as As(V) and its sorption to goethite and amorphous iron oxide is more favorable than that of As(III) below pH 5–6, whereas above pH 7–8 As(III) has a higher affinity for solids (Dixit and Hering, 2003).

### 3.4. Assessment of contamination of stream sediments before the remediation

The degree of pollution caused by heavy metals in stream sediments has been classified using a geoaccumulation index



**Fig. 7.** Correlations between metals and also As from upstream and downstream sediments, before the remediation, from the Senhora das Fontes old uranium mine area. The highest U concentration of 834 mg/kg is an outlier and was not plotted in the diagrams, but it was included for r-correlation coefficient.

(Igeo) defined by Müller (1979).  $I_{geo} = \log_2[Cn/(1.5) \cdot Bn]$ , where Cn = chemical element concentration (ppm) and Bn = background levels (ppm). Median data from a low density geochemical survey of Portuguese stream sediments were used to define background values for heavy metals and the metalloid As (Ferreira, 2000; Ferreira et al., 2001). The calculated Igeo for upstream and downstream sediments, before the remediation, are given in Appendix E a, b. These stream sediments are mainly contaminated in As, Mn, Th and U. In upstream sediments, As and Mn reached the class 3 (moderately to heavily contaminated), U and Th reached the classes 4 (heavily contaminated) and 5 (heavily to extremely contaminated), respectively. In downstream sediments, Mn and Th reached the same class as in upstream sediments, but As and U reached a higher class 4 and 6 (extremely contaminated), respectively, than in upstream sediments, because the downstream sediments received the direct effect of dumps.

The median values and maximum concentrations of Co, Cr, Cu, Fe, Mn, Th and U of these Portuguese stream sediments are higher than those of stream sediments from Pinhal do Souto uranium mine area (Table 5). As for the soils, the contamination of these stream sediments derives from the exploration of the old Senhora das Fontes uranium mine and the U removal processes from ores of

this mine and nearby mines and accumulation of waste materials, decantation muds, dissolved waste precipitation and ore dissolution from the open pit in seven dumps which released metals, metalloid and radionuclides due to leaching.

### 3.5. The effect of remediation on textural characteristics and physical-chemical parameters of stream sediments

The stream sediment samples collected after the remediation contain mainly sand and silt fractions and a minor clay (<4 μm) fraction less than 5.4%. In general, the silt and clay size fractions increase and the sand fraction decreases from before to after the remediation (Appendix D). After the remediation, the mineralogy of the <2 μm clay size fraction contains 46–64% of illite, 16–42% of kaolinite, 0–24% of vermiculite, 0–9% of chlorite and only one sample has 3% of montmorillonite. Therefore, the significant difference found is in kaolinite (16–42%), showing a larger range and reaching a higher value after the remediation than before the remediation (24–29%). The studied samples have low quantities of silt and clay and the clay mineral association has a general low adsorption capacity for contaminants, except montmorillonite.

**Table 5**  
Comparison of metal and metalloid contents (mg/kg), except Fe (%), obtained by aqua regia digestion of stream sediments, before and after the remediation, from the Senhora das Fontes old uranium mine area with those of another Portuguese uranium mine area.

	S. Fontes: before the remediation			S. Fontes: after the remediation			Pinhal do Souto (1)		
	Median	Maximum	N	Median	Maximum	N	Median	Maximum	N
As	65.0	153	34	82.1	153	26	89.1	194	15
Co	7.1	18.9	34	8.5	31.6	26	0	15.2	15
Cr	22.1	44.7	34	21.8	39.9	26	0	21.5	15
Cu	13.6	54.8	34	13.7	48.1	26	4.3	20.8	15
Fe	1.4	3.0	34	2.0	3.5	26	0.83	2.05	15
Mn	551	4384	34	484	1478	26	269	1243	15
Ni	14.9	36.9	34	18.3	49.6	26	0	98.4	15
Pb	21.0	89.0	34	21.4	41.1	26	37.2	137	15
Th	78.3	180	34	104	179	26	32.6	98.4	15
U	19.6	834	34	51.2	106	26	0	35.7	15
Zn	57.4	197	34	69.2	140	26	100.4	234	15

(1) Neiva et al. (2014); N-number of determinations.



In the upstream sediments, the pH values range between 4.3 and 5.7 before the remediation and between 3.8 and 5.5 after the remediation (Appendix D). In the downstream sediments, the pH values range between 4.3 and 6.6 before the remediation and between 3.6 and 6.9 after the remediation. Therefore, mainly the pH of stream sediments reaches lower values after the remediation, because the pH values of surface water decreased after remediation (Neiva et al., 2015). The electrical conductivity (EC) of upstream sediments ranges from 13 to 55  $\mu\text{S}/\text{cm}$  before the remediation and between 20 and 89  $\mu\text{S}/\text{cm}$  after the remediation (Appendix D), showing a general increase. In the downstream sediments, EC ranges from 13 to 534  $\mu\text{S}/\text{cm}$  before the remediation and from 22 to 152  $\mu\text{S}/\text{cm}$  after the remediation, and the highest value decreased, and the same occurred in surface water after the remediation (Neiva et al., 2015). In general, CEC and OM increase in upstream and downstream sediments after the remediation (Appendix D).

### 3.6. The effect of remediation on metals and metalloids of stream sediments

In general, after the remediation, Al, Fe, As, Cr, Ni, Th, U and Zn concentrations increase in upstream and downstream sediments (Fig. 8, Appendix D). After the remediation, Al, As, Th and U concentrations increased in the upstream surface water, but As, Cr, Ni, U and Zn concentrations decreased in downstream surface water (Neiva et al., 2015). The increases in Al, metalloid and radionuclides concentrations in upstream surface water may eventually be due to an unreported problem related to the decantation lake located at SW to receive the waters that percolated the accumulated materials in the temporary deposit during the remediation. The decreases in metalloid, metals and radionuclides concentrations in downstream surface water are due to the effect of remediation. But the downstream surface water was still contaminated (Neiva et al., 2015). In general, the increases of Al, As, Th and U concentrations in upstream sediments after the remediation are explained by the behavior of Al, metalloid and radionuclides in upstream surface water. The arsenic concentration increases up to 6 times in the upstream sediment sample SD19 and up to 2 times in three other upstream sediment samples SD24, SD28 and SD30. The highest increase occurs in the U concentration up to 73 times in the upstream sediment sample SD19. But U concentration decreases up to 32 times in the downstream sediment sample SD39 close to the dumps area (Fig. 2, Appendix D) and also up to 2 times in two other downstream sediment samples SD13 and SD7. These behaviours of U concentration in downstream sediments are also supported by the behaviour of U in the downstream surface water.

The main reason for the increase in metals, metalloid and radionuclides concentrations in upstream and downstream sediments after the remediation is the relocation of mine dumps that implied to move all materials twice, as they went first to a temporary deposit and afterwards to the present deposit. The remobilization exposed uranium minerals like autunite, uraninite and Fe-saléite and sulphides (pyrite, arsenopyrite, sphalerite and chalcopyrite) from quartz veins and also of tailings. In general, tailings have high concentrations of metals and metalloids due to sulphide oxidation and the subsequent redistribution of trace metals and metalloids by secondary Fe precipitates and phases formation (Carlsson et al., 2002; Heikkinen and Räsänen, 2009). The weathering of sulphides, due to oxidation and water infiltration causes a decrease in pH, as observed in the stream sediments of the studied area after the remediation (Appendix D), and consequently the mobilization of metals, metalloid and radionuclides in stream water and their distribution between the aqueous phase and stream sediments. However, only a small portion of free metal ions remain dissolved in water and there is a significant retention

of metals and metalloids in stream sediments (Macklin, 1992) and also radionuclides, as observed in the Senhora das Fontes mine area.

The increase of Fe, Cr, Ni and Zn concentrations in upstream and downstream sediments and the increase in Al, As, Th and U concentrations in downstream sediments are also explained by the relocation process of dumps. Zinc concentration increases up to 31 times in a downstream sediment sample, while Ni concentration increases up to 10 and 7 times in downstream and upstream samples, respectively (Appendix D). In the downstream sediment samples, As increases up to 2 times in SD31 and U increases mainly up to 2 times, but also up to 3 times in SD5 and SD31 and up to 4 times in SD43. The remediation ended in January 2011. After the remediation, the analyzed water samples were collected at May and June 2011 and stream sediments were collected at October 2013. The contact of rainwater within materials from the tailings due to the relocation of dumps and the continuous flow of upstream and downstream surface water explain the enrichment found in metals, metalloid and radionuclides. In general, after the remediation, Al, As, Cu, Mn, Ni, Th, U and Zn have higher concentrations in downstream sediments than in upstream sediments (Appendix D), which can be similarly explained by the continuous flow of contaminated surface water.

The good correlations found for some metals and also As from upstream and downstream sediments after the remediation (Fig. 9) suggest that U(VI), Th and As(V) can be adsorbed to Fe-oxyhydroxides, as found in stream sediments before the remediation.

### 3.7. The effect of remediation on the contamination of stream sediments

The upstream and downstream sediment samples collected after the remediation are mainly contaminated in As, Th and U (Appendix E a, b). After the remediation, the As in upstream sediment samples reaches a higher class of contamination 4 (heavily contaminated) than before the remediation, being this class more frequent in downstream sediment samples than before the remediation. The class 5 (heavily to extremely contaminated) is more frequent for Th in upstream and downstream sediment samples after than before the remediation. The U reaches the class 5 in an upstream sediment sample and in several downstream sediment samples after the remediation. However, the class 6 (extremely contaminated) was reached with U in two downstream sediment samples before the remediation. Upstream sediment samples that were practically uncontaminated in U before the remediation reached the classes 2, 3, 4 and 5 after the remediation. In general, the class of contamination in U increased in downstream sediment samples after the remediation.

The increase in As, Th and U contamination of upstream and downstream sediments is due to the effect of surface water. However, the reaction of water with the weathering products of sulphides and uranium minerals from pieces of quartz veins and of tailings that were exposed during the remediation are responsible for the more intense contamination in downstream sediments about two years after the waters have been collected and two years and nine months after the remediation process has been finished.

The median values of As, Co, Fe, Ni, Th, U and Zn concentrations of stream sediments from the Senhora das Fontes uranium mine area are higher after than before the remediation (Table 5). But the highest concentration of most metals decreased after the remediation, except for As, Co, Fe and Ni that increased. The median values of Co, Cr, Cu, Fe, Mn, Ni, Th and U concentrations and the highest concentrations of Co, Cr, Cu, Fe, Mn, Th and U of stream sediments after the remediation are higher than those of median values and

the highest concentrations, respectively, of stream sediments from Pinhal do Souto (Table 5).

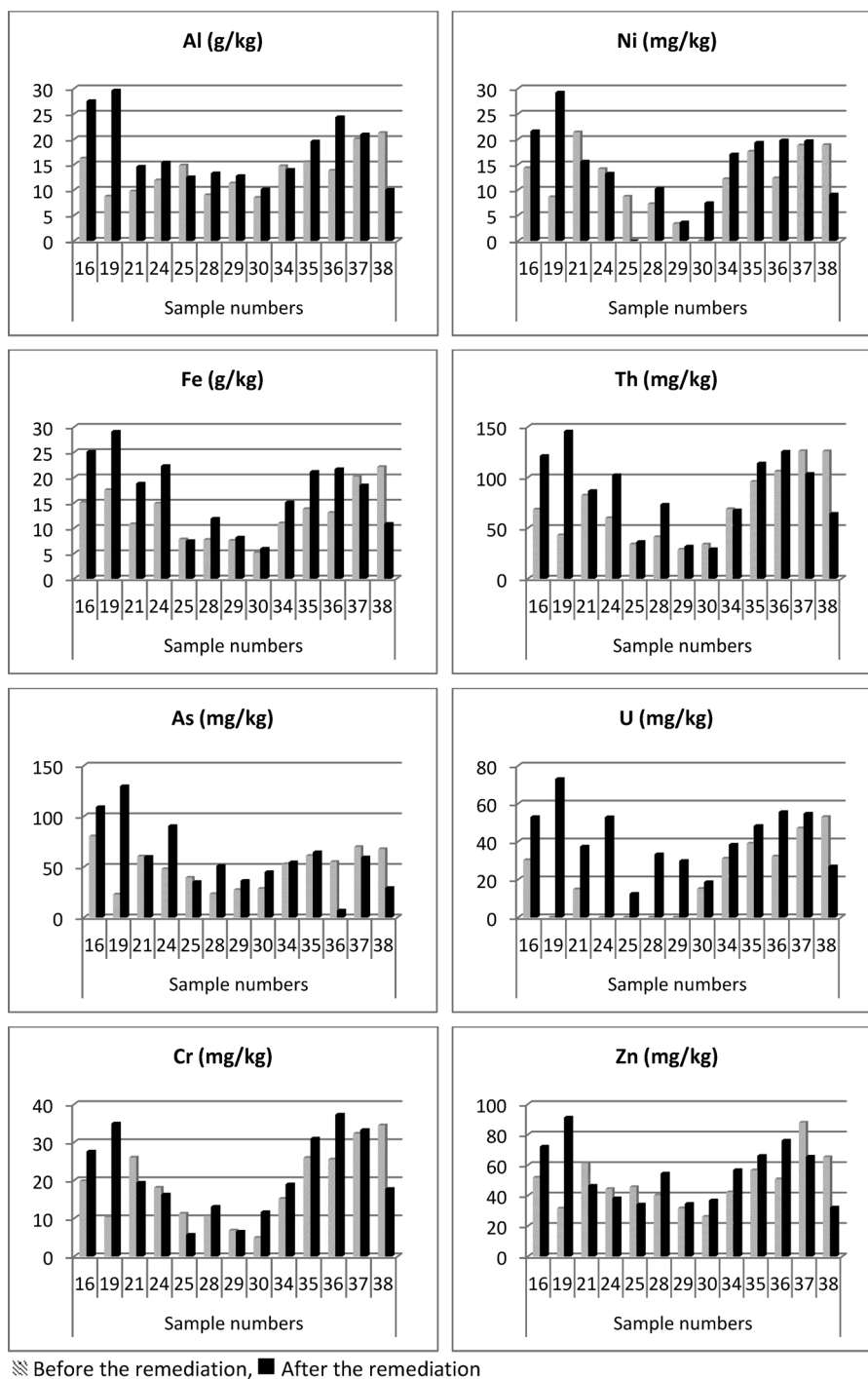
#### 4. Conclusions

Before the remediation, Al, As, Co, Cr, Cu, Fe, Ni, Sr, Th, U and Zn concentrations in soils from inside the mine influence area are higher than those in soils from outside this area due to radionuclides, metals and metalloid released from the mine dumps. In general, the PCA shows a distinction between soil samples from

inside and outside the mine influence area. Metals, U(VI) and As(V) from soils can be adsorbed by Fe-oxyhydroxides and the humic acid increases the U uptake, because the pH of soils is lower than 7. Soils are contaminated in As, Co, Cd, Ni and U and must not be used for public or private green and residential areas.

Before the remediation, Al, As, Cu, Mn, Ni, Pb, U and Zn concentrations are higher in downstream sediments than in upstream sediments, due to erosion and percolation of water through the mine dumps. A distinction between upstream and downstream sediments is also shown by the PCA. The good positive correlations

##### a. Upstream:



**Fig. 8.** Diagrams for metals and As in upstream and downstream sediments, before and after the remediation, from the Senhora das Fontes old uranium mine area. a. Upstream sediments; b. downstream sediments.

## b. Downstream:

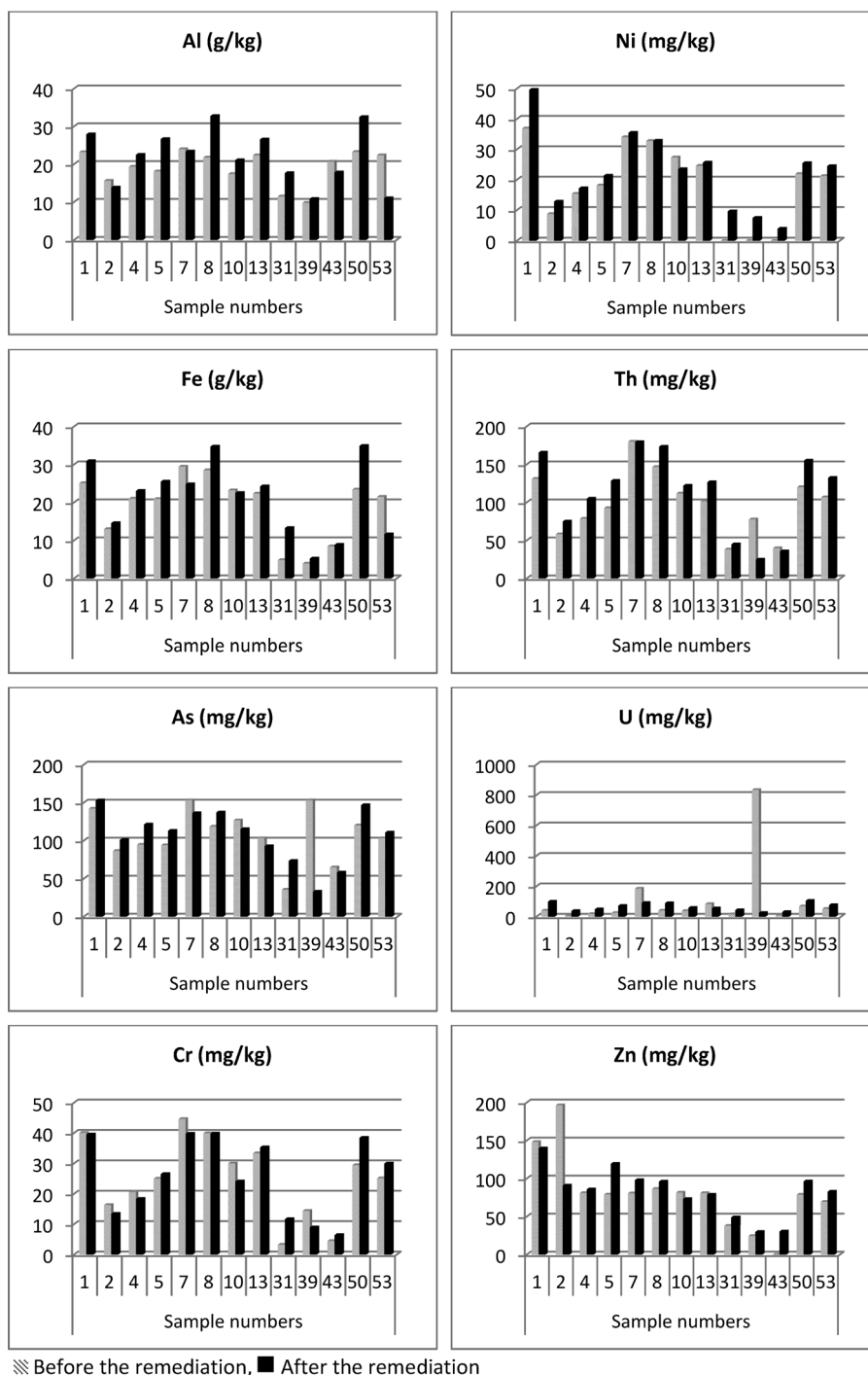
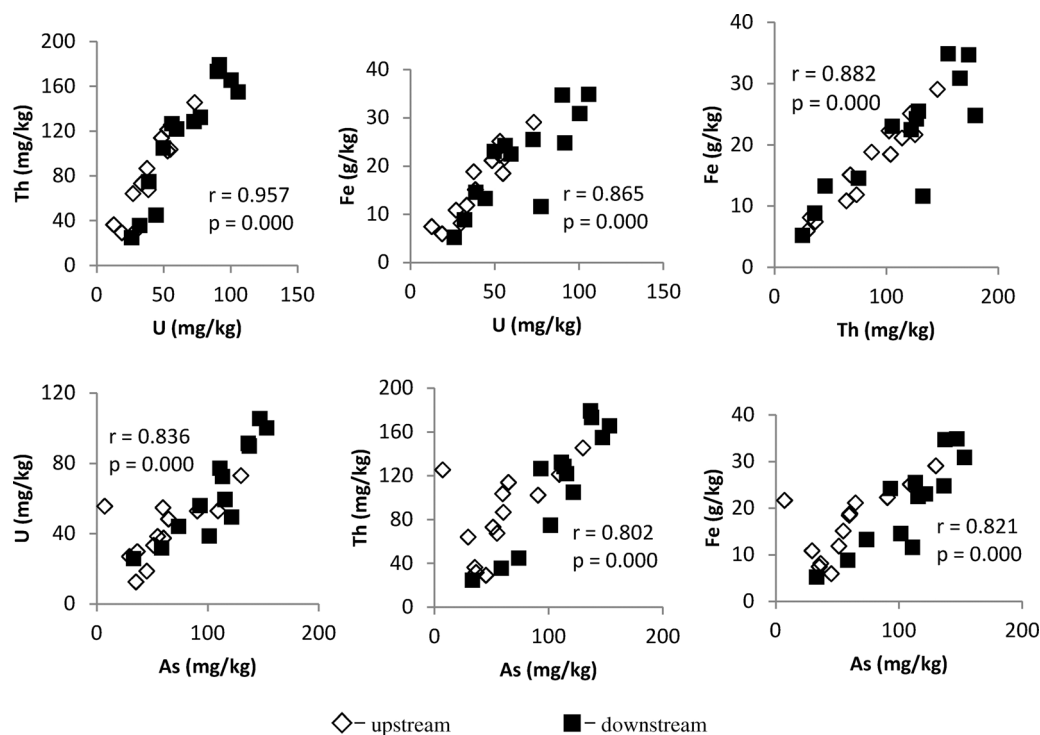


Fig. 8. (Continued)

of Fe vs U, Fe vs Th and Fe vs As for upstream and downstream sediments suggest that U(VI), Th and As(V) can be adsorbed by Fe-oxhydroxides. Algae may promote the reduction of U(VI) to U(IV) and the latter will be oxidized in contact with the air. The pH conditions of stream sediments are favorable to the As(V) occurrence. The stream sediments are mainly contaminated in As, Mn, Th and U. In general, downstream sediments are more contaminated in U and As than upstream sediments, because U and As leached from dumps were carried by surface water to downstream sediments.

In general, after the remediation, the pH of sediments reaches lower values. The Al, Fe, As, Cr, Ni, Th, U and Zn concentrations are higher in upstream and downstream sediments than before the remediation, due to the relocation of dumps. This effect also caused higher concentrations of Al, As, Cu, Mn, Ni, Th, U and Zn in downstream than in upstream sediments. Metals and the metalloid were transported by surface water. The U(VI), Th and As(V) can be adsorbed to Fe-oxhydroxides, because Fe shows good correlations with them. After the remediation, the contamination in U, Th and As of stream sediments increased and generally more inten-



**Fig. 9.** Correlations between metals and also As from upstream and downstream sediments, after the remediation, from the Senhora das Fontes old uranium mine area.

sively downstream. This work highlights the danger and impact on stream sediments of relocating dumps during a remediation process. A temporary deposit must be avoided during this process, because it implies more relocation of all materials. The remobilization exposes uranium minerals and sulphides from quartz veins and tailings and they will be weathered causing more environmental contamination. Any accident with decantation lakes must be reported and its effects carefully treated. It is so advisable that, when necessary, additional protection actions should be undertaken when relocating contaminated material in order to avoid to widespread contamination.

#### Acknowledgements

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#### Appendix A. Textural and mineralogical characteristics of representative soil samples, before the remediation, from the Senhora das Fontes old uranium mine area

Samplenumbers	Textural characteristics			Mineralogical characteristics		Fraction <63 $\mu\text{m}$		Fraction <2 $\mu\text{m}$			
	% Clay	% Silt	% Sand	Quartz	MuscoviteIllite	K-feldspar	Albite	Illite	Kaolinite	Fe-chlorite	Vermiculite
Samples outside the old mine influence area											
SL-40	3.3	37.9	58.8	11	73	5	11	31	57	–	11
SL-44	2.0	23.9	74.1	14	68	4	14	46	50	–	4
Samples inside the old mine influence area											
SL-3	2.4	25.2	72.4	21	72	–	7	57	43	–	–
SL-5	2.4	28.4	69.2	17	49	14	20	74	26	–	–
SL-7	3.4	40.1	56.5	27	61	4	8	38	62	–	–
SL-8	2.6	22.3	75.1	100	–	–	–	43	57	–	–
SL-10	2.6	35.2	62.2	12	78	2	8	54	46	–	–
SL-13	3.2	38.7	58.1	16	84	–	–	69	31	–	–
SL-14	0.74	10.2	89.1	9	80	–	11	33	67	–	–
SL-15	n.d.	n.d.	n.d.	27	55	4	14	47	33	10	9
SL-16	1.11	7.6	91.3	21	56	15	8	30	42	–	28
SL-21	n.d.	n.d.	n.d.	22	64	–	14	35	65	–	–
SL-23	2.7	22.3	75.0	23	44	21	12	6	17	–	28
SL-26	3.8	49.5	46.7	9	88	–	3	29	71	–	–

– not found; n.d.—not determined

## Appendix B. Physical-chemical parameters and concentrations of metals and metalloids of soils, before the remediation, from the Senhora das Fontes old uranium mine area

	Physical-chemical parameters					Trace metals and metalloids															
	OM	CEC	pH	Temp	EC	Al (g/kg)	Fe (g/kg)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	Th (mg/kg)	U (mg/kg)	Zn (mg/kg)	
Samples from outside the old mine influence																					
SL-2	1.36	0.66	4.6	18.3	34	22.7	7.7	53.3	*	*	8.1	*	408	5.7	13.0	24.7	10.3	53.1	3.5	40.0	
SL-28	0.85	0.89	4.9	22.9	22	7.5	4.5	29.9	*	*	2.7	*	298	3.6	13.0	*	5.1	24.1	*	23.2	
SL-29	1.02	1.00	4.8	21.9	16	7.5	5.0	24.0	*	*	4.4	*	118	4.2	8.9	*	6.2	24.3	5.0	20.7	
SL-30	nd	nd	4.9	16.0	52	5.7	10.5	34.5	*	3.5	8.2	11.4	645	8.7	41.4	*	14.9	27.9	1.60	60.2	
SL-31	3.6	2.9	5.1	14.4	29	14.7	6.4	21.0	*	2.9	8.0	*	466	10.3	14.4	4.8	10.9	21.3	12.1	30.6	
SL-32	nd	nd	4.3	23.0	38	9.8	5.5	18.1	*	*	0.76	*	120	2.7	12.2	*	5.8	13.9	*	30.7	
SL-33	nd	nd	5.3	21.3	13	8.0	7.0	18.7	*	3.2	5.5	*	237	7.6	11.4	*	8.7	21.8	29.7	26.6	
SL-34	nd	nd	5.1	22.9	22	9.5	6.2	38.0	*	*	5.0	*	262	5.0	12.5	*	6.3	41.1	32.0	32.9	
SL-35	0.48	0.63	5.3	21.2	8	11.0	6.2	30.8	*	*	4.5	*	264	5.0	12.9	*	6.3	35.2	26.0	33.1	
SL-36	0.67	0.33	4.5	22.1	21	11.2	10.1	26.1	*	3.9	8.7	4.8	160	8.9	14.4	*	5.8	36.0	24.5	33.0	
SL-37	nd	nd	6.0	13.4	28	22.0	30.4	90.0	*	15.3	31.1	23.7	257	26.7	16.6	*	25.3	114	42.1	66.8	
SL-38	nd	nd	6.2	21.2	13	23.5	30.4	70.6	*	14.1	31.2	24.1	213	24.9	16.0	*	15.7	120	23.3	71.2	
SL-39	nd	nd	4.9	16.3	23	19.1	8.3	31.1	*	*	5.2	*	199	5.7	14.9	*	5.6	19.3	3.4	23.6	
SL-40	0.78	3.6	5.5	21.5	13	33.2	33.8	75.6	2.0	15.8	37.4	23.3	132	32.1	21.7	6.7	10.6	142	39.7	78.4	
SL-41	1.59	2.3	5.3	14.5	28	24.6	22.6	47.6	*	10.2	23.2	12.0	576	22.5	17.9	*	12.5	94.3	8.8	50.2	
SL-42	1.60	0.39	4.9	21.4	32	13.7	12.0	33.4	*	6.4	12.3	6.2	540	11.7	18.3	5.5	7.2	55.7	*	35.7	
SL-43	nd	nd	5.9	14.8	88	29.4	29.7	74.3	2.0	13.7	36.2	23.6	2028	27.2	26.4	*	32.0	123	32.1	90.3	
SL-44	2.5	4.1	5.1	19.3	54	29.3	30.8	66.5	2.0	14.3	46.8	15.4	1634	20.9	21.3	*	11.5	182	14.7	74.6	
SL-45	nd	nd	4.3	21.6	23	8.3	5.8	12.4	*	*	2.3	*	324	3.8	25.1	*	5.1	16.6	1.52	25.1	
SL-46	nd	nd	6.9	15.0	25	7.4	5.5	17.6	*	*	*	*	172	*	11.5	*	8.2	14.7	*	22.5	
Samples from inside the old mine influence area																					
SL-1	nd	nd	4.9	18.6	24	22.7	27.2	111	*	17.0	29.6	19.9	866	22.8	18.1	*	22.6	127	41.9	66.7	
SL-3	3.9	8.0	6.4	15.9	77	11.1	37.0	147	*	17.0	46.8	53.2	883	36.5	38.0	4.4	26.5	185	77.6	111	
SL-4	1.95	1.85	4.6	18.6	90	12.8	14.6	90.3	*	24.9	86.7	*	573	12.7	11.0	*	18.2	79.1	15.1	53.2	
SL-5	1.55	0.73	4.3	18.6	45	12.3	11.6	55.1	*	5.2	12.4	12.1	332	10.4	15.7	*	10.8	65.2	78.2	51.0	
SL-6	nd	nd	4.7	18.6	47	19.7	19.1	105	*	10.3	30.4	18.8	710	22.7	19.5	*	12.3	102	10.7	59.8	
SL-7	1.17	2.7	5.0	18.1	25	25.8	28.7	107	*	12.4	34.8	26.4	942	28.3	16.9	*	9.9	157	57.2	70.6	
SL-8	1.21	6.2	5.4	18.6	41	33.1	41.0	120	*	21.0	49.6	51.0	1207	31.3	39.3	*	13.0	213	51.2	87.3	
SL-9	2.8	5.1	5.4	22.6	83	21.4	19.3	98.1	*	8.2	17.5	*	483	12.8	30.3	*	13.7	105	24.4	63.4	
SL-10	1.88	6.6	6.1	22.4	64	27.7	45.1	175	*	14.2	30.5	55.7	1585	30.5	30.4	*	15.2	160	71.6	96.7	
SL-11	nd	nd	6.3	16.3	57	29.4	32.9	155	*	17.0	37.7	42.4	993	38.8	36.9	*	27.2	157	48.5	133	
SL-12	nd	nd	5.5	15.9	86	26.8	27.0	143	*	22.1	38.3	49.1	960	49.8	39.6	*	20.9	164	59.4	134	
SL-13	2.1	6.1	5.3	22.0	39	37.9	43.8	198	*	29.9	49.3	92.1	1263	57.6	42.9	*	23.3	222	53.7	140	
SL-13'	nd	nd	6.0	22.9	31	41.3	45.9	195	*	22.3	52.7	49.0	1180	46.1	31.1	*	22.3	227	63.5	108	
SL-14	7.3	8.0	5.9	15.9	77	25.5	48.1	281	*	25.0	42.8	47.3	2080	119	48.8	4.9	41.5	203	89.1	160	
SL-15	1.07	2.9	5.2	15.9	26	33.4	30.8	375	*	18.7	34.1	37.8	655	26.5	33.2	4.6	24.2	174	72.0	70.7	
SL-16	1.03	1.92	5.5	15.5	37	30.7	21.2	209	*	7.9	25.2	22.7	397	23.9	35.5	5.9	12.0	102	94.6	69.7	
SL-17	5.0	3.2	4.1	21.5	68	27.0	13.3	169	*	7.2	11.4	*	221	18.7	33.6	*	14.2	60.0	17.1	63.7	
SL-18	1.66	3.3	5.4	21.9	49	23.0	25.1	232	*	12.9	31.3	21.9	913	28.8	34.6	*	18.4	138	38.6	82.5	
SL-19	1.07	2.0	5.0	22.9	36	31.8	22.0	320	*	10.3	24.7	16.0	634	23.1	25.4	5.6	14.0	115	67.2	8.6	
SL-21	1.45	6.3	5.4	22.8	22	29.9	36.3	201	*	15.4	42.0	28.4	524	38.8	20.7	*	30.3	172	54.3	89.7	
SL-22	nd	nd	5.7	22.7	20	20.8	35.9	200	*	18.8	32.5	59.2	567	36.6	31.6	*	23.3	146	55.8	103	
SL-23	2.4	20.5	4.9	21.8	74	29.1	31.4	185	3.0	19.4	93.1	37.5	413	61.8	24.0	*	45.5	145	92.5	92.7	
SL-24	1.05	4.6	5.3	22.5	17	18.0	15.0	73.9	*	4.0	11.1	26.7	926	10.5	24.1	*	14.1	60.7	36.6	75.9	
SL-25	4.3	8.0	6.7	23.2	155	27.6	28.7	208	3.0	18.6	36.0	35.0	951	31.4	33.3	*	29.8	146	38.7	110	
SL-26	1.50	6.0	5.8	22.6	31	39.1	36.0	155	4.0	21.3	45.8	50.4	638	42.7	34.3	7.3	17.3	186	42.7	90.4	
SL-27	2.6	3.6	5.0	21.9	42	13.5	9.8	50.9	*	4.5	10.5	6.7	404	9.7	20.4	*	13.7	43.3	*	46.2	
SL-47	nd	nd	5.1	24.0	39	15.5	22.0	85.9	2.0	13.0	26.3	25.5	821	20.4	23.3	*	8.1	94.2	14.3	69.3	
SL-51	nd	nd	5.6	22.9	32	19.1	19.1	91.1	2.0	7.9	19.8	14.3	519	13.3	25.0	*	14.1	67.0	15.4	71.5	

OM—organic matter (%); CEC—cation exchange capacity (cmol/kg); temp—Temperature (°C); EC—electrical conductivity ( $\mu\text{S}/\text{cm}$ ); \*—below detection limit; nd—not determined. Analyst: A.C.T.Santos.

### Appendix C. Textural characteristics, physical-chemical parameters, metals and metalloids of upstream sediments collected, before the remediation, from the Senhora das Fontes old uranium mine area

	Textural characteristics			Physical-chemical parameters				Trace metals and metalloids														
	% Clay	% Silt	% Sand	pH	EC (µS/cm)	CEC (cmol/kg)	OM %	Al (g/kg)	Fe (g/kg)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	Th (mg/kg)	U (mg/kg)	Zn (mg/kg)
SD 14	nd	nd	nd	4.8	94	nd	nd	15.1	16.0	76.5	*	5.7	23.6	20.6	244	15.8	24.4	*	16.5	67.6	20.5	68.0
SD 17	0.81	9.0	89.1	4.7	17	2.6	1.62	8.5	7.9	24.6	*	*	7.0	*	175	5.7	13.4	*	9.1	31.3	*	31.2
SD 18	1.11	10.7	86.9	5.8	18	4.4	0.72	20.0	28.5	71.7	*	10.8	31.1	24.2	394	22.3	12.0	*	18.6	105.5	16.7	65.6
SD 20	0.56	5.4	93.3	6.2	17	3.6	0.43	12.9	8.7	53.4	*	9.3	23.5	19.5	457	18.9	17.5	*	11.6	84.9	15.0	52.2
SD 23	2.6	23.1	72.0	4.8	38	2.5	2.3	11.3	9.4	46.4	*	4.6	18.8	11.5	809	13.00	19.2	*	14.7	53.3	5.0	58.0
SD 27	0.60	7.0	91.5	5.0	23	0.86	1.90	5.5	3.6	7.3	*	*	2.3	*	615	*	14.3	*	7.9	13.8	*	23.3
SD 32	2.1	20.1	75.6	5.2	28	4.8	2.7	21.9	22.6	78.1	2.5	10.7	39.1	15.6	443	23.5	25.3	*	13.6	152.6	57.5	69.1
SD 52	2.5	15.5	83.0	4.9	7	0.15	1.17	9.5	5.2	34.3	*	*	4.2	*	75.1	*	10.3	*	5.7	32.3	13.2	26.1

EC—electrical conductivity; CEC—cation exchange capacity; OM—organic matter; \*—below detection limit; nd—not determined. Analyst: A.C.T.Santos.

### Appendix D. Textural characteristics, physical-chemical parameters, metals and metalloids of stream sediments, before and after remediation, from the Senhora das Fontes old uranium mine area.

	Textural characteristics			Physical-chemical parameters				Trace metals and metalloids															
	% clay	% silt	% sand	pH	EC (µS/cm)	CEC (cmol/kg)	OM (%)	Al (g/kg)	Fe (g/kg)	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	Th (mg/kg)	U (mg/kg)	Zn (mg/kg)	
upstream																							
SD 16 a	nd	nd	nd	4.9	38	nd	nd	16.2	15.1	80.3	*	9.6	19.8	14.2	565	14.3	17.2	*	12.1	68.6	30.3	51.9	
SD 16 b	nd	nd	nd	5.1	64	nd	nd	27.5	25.1	109	*	10.1	27.6	22.3	899	21.6	19.9	*	17.5	121	53.0	72.2	
SD 19 a	0.03	0.23	99.7	5.7	13	1.21	0.40	8.7	17.6	22.9	*	4.4	10.4	*	201	8.6	8.1	*	10.4	43.1	*	31.6	
SD 19 b	4.5	34.7	60.1	5.4	74	5.5	2.9	29.6	29.1	130	*	10.2	35.0	29.6	946	29.2	41.1	*	18.1	146	73.0	91.3	
SD 21 a	2.6	20.2	75.2	4.9	30	2.0	2.4	9.7	10.8	60.5	*	11.1	26.0	14.4	647	21.4	19.1	*	12.4	82.3	14.9	61.3	
SD 21 b	3.1	25.4	71.5	5.3	25	14.1	1.69	14.6	18.8	60.1	*	7.4	19.4	12.7	494	15.6	12.6	*	13.2	86.8	37.4	46.5	
SD 24 a	nd	nd	nd	4.3	30	nd	nd	11.9	14.9	47.9	*	8.6	18.1	12.1	1918	14.1	39.2	*	10.2	60.0	*	44.4	
SD 24 b	nd	nd	nd	4.4	20	nd	nd	15.4	22.3	90.5	*	5.6	16.3	*	185	13.2	22.9	*	8.3	102	52.9	38.3	
SD 25 a	nd	nd	nd	4.9	41	nd	nd	14.9	7.8	39.4	*	*	11.3	*	564	8.7	21.7	*	14.5	34.1	*	45.6	
SD 25 b	nd	nd	nd	4.9	20	nd	nd	12.5	7.4	35.2	*	*	5.7	*	134	*	12.4	*	8.2	36.5	12.6	34.2	
SD 28 a	nd	nd	nd	5.0	13	nd	nd	9.0	7.7	23.3	*	4.0	10.6	*	1374	7.2	12.5	*	9.6	41.2	*	40.3	
SD 28 b	nd	nd	nd	3.8	27	nd	nd	13.3	11.9	51.1	*	*	13.1	*	386	10.3	15.6	*	7.3	73.3	33.3	54.6	
SD 29 a	1.45	8.7	88.7	4.8	16	0.97	0.59	11.3	7.5	27.4	*	2.6	6.8	3.3	384	3.3	13.1	*	8.9	28.9	*	31.7	
SD 29 b	3.4	27.6	69.0	4.1	84	9.0	3.3	12.8	8.1	36.4	*	*	6.5	*	226	3.6	15.7	*	*	31.9	29.9	34.7	
SD 30 a	1.07	8.0	89.9	4.3	16	0.39	0.78	8.5	5.1	28.5	*	*	4.9	*	100	*	13.1	*	6.3	34.0	15.1	26.2	
SD 30 b	3.4	27.7	68.9	4.4	21	5.1	1.62	10.2	6.0	44.9	*	*	11.7	*	126	7.4	12.8	*	10.6	29.3	18.7	36.9	
SD 34 a	2.7	16.5	79.1	5.3	16	3.2	0.86	14.7	11.0	52.8	*	4.1	15.2	8.5	2588	12.2	17.2	*	7.5	69.0	31.2	42.3	
SD 34 b	1.83	17.4	80.8	5.1	89	13.0	6.4	14.0	15.1	54.7	*	7.5	19.0	*	979	17.0	15.4	*	18.4	67.7	38.5	56.8	
SD 35 a	1.75	13.0	85.2	4.6	55	0.66	4.7	15.5	13.8	61.0	*	6.0	25.9	10.9	738	17.6	30.9	*	10.0	95.8	39.0	56.7	
SD 35 b	2.9	30.2	67.0	5.5	57	16.5	3.2	19.6	21.1	64.6	*	7.5	31.0	12.9	201	19.3	21.5	*	8.2	114	48.3	66.4	
SD 36 a	1.15	10.3	87.0	5.7	48	2.4	1.41	13.8	13.0	55.1	*	4.4	25.5	8.8	195	12.3	17.0	*	12.8	106	32.3	50.8	

SD 36 b	2.2	20.5	77.3	4.4	48	8.0	4.1	24.4	21.7	7.0	*	10.3	37.3	14.4	228	19.8	27.2	*	14.5	126	55.6	76.2
SD 37 a	2.3	16.9	78.6	5.3	47	4.4	2.5	20.0	20.2	69.8	2.0	9.0	32.3	14.4	587	18.8	43.0	*	14.4	126	47.1	88.0
SD 37 b	3.4	31.0	65.5	4.4	48	12.1	3.5	21.0	18.5	59.5	*	6.8	33.3	12.8	173	19.6	22.5	*	13.9	104	54.8	65.6
SD 38 a	1.80	18.6	77.0	4.9	55	5.6	2.2	21.2	22.1	67.7	1.92	8.2	34.5	13.0	209	18.9	22.6	*	16.4	126	53.1	65.3
SD 38 b	2.2	18.0	79.8	4.7	34	12.2	2.7	10.1	10.9	29.4	*	4.9	17.8	6.5	155	9.1	8.4	*	7.0	64.2	27.0	32.2
downstream																						
SD 1 a	3.0	28.0	65.5	4.8	534	5.8	5.2	23.2	25.1	142	3.4	18.9	40.1	54.8	3921	36.9	28.2	*	19.9	131	41.0	148
SD 1 b	2.6	24.1	73.4	6.5	65	11.7	2.4	27.9	30.9	153	*	31.6	39.6	48.1	1239	49.6	28.3	*	14.5	166	100	140
SD 2 a	0.38	3.5	95.6	6.6	168	5.2	4.6	15.6	13.0	86.7	*	5.5	16.3	51.0	2568	8.8	89.0	*	25.3	58.3	5.3	197
SD 2 b	1.15	9.8	89.0	6.9	34	5.4	2.8	13.9	14.6	101	*	4.8	13.4	27.8	585	12.8	28.2	*	18.1	75.1	38.7	91.0
SD 4 a	0.14	0.75	99.1	6.2	22	0.76	0.84	19.4	21.0	94.9	*	9.4	20.6	23.2	665	15.4	29.3	*	17.5	78.8	18.7	81.2
SD 4 b	1.11	9.6	89.3	6.5	28	6.1	1.93	22.5	23.1	121	*	10.0	18.3	21.4	960	17.2	22.4	*	18.7	105	49.6	86.0
SD 5 a	2.0	20.4	75.4	4.5	106	3.1	3.5	18.1	20.9	94.2	*	10.0	25.0	25.3	491	18.2	21.6	*	14.5	92.7	26.0	79.1
SD 5 b	2.2	21.5	76.4	6.3	40	6.3	5.6	26.7	25.5	113	*	11.5	26.6	28.6	645	21.4	29.9	*	16.1	129	72.6	119
SD 7 a	2.2	21.1	72.8	6.0	78	4.7	1.22	24.0	29.4	153	*	17.9	44.7	39.8	778	34.0	14.6	3.9	12.3	180	186	80.7
SD 7 b	2.5	28.9	68.6	5.9	51	3.6	1.60	23.4	24.8	136	*	16.0	39.8	42.0	477	35.5	21.3	*	11.0	179	91.5	98.2
SD 8 a	0.55	4.8	93.9	6.3	13	2.9	0.28	21.8	28.5	119	*	16.8	40.0	39.8	4301	32.8	26.3	*	12.4	147	40.8	86.5
SD 8 b	2.2	27.8	70.0	6.4	26	8.8	2.6	32.8	34.7	137	*	19.1	39.9	43.7	830	32.9	21.2	*	12.5	174	90.0	96.2
SD 10 a	2.4	22.8	72.6	5.7	61	5.6	2.9	17.4	23.2	127	*	16.8	30.0	27.3	4384	27.4	20.9	*	17.3	112	38.5	81.7
SD 10 b	3.3	28.1	68.6	5.9	32	9.8	2.9	21.1	22.5	115	*	12.6	24.1	21.8	918	23.5	24.6	*	13.4	122	59.5	73.2
SD 13 a	2.0	20.9	75.1	4.8	110	3.8	3.2	22.4	22.4	103	*	11.8	33.4	25.8	537	24.6	31.4	*	15.7	102	84.3	81.0
SD 13 b	5.4	48.1	46.5	4.7	35	7.3	3.5	26.6	24.3	92.9	*	9.4	35.3	23.2	362	25.7	26.6	*	12.8	127	56.0	78.9
SD 31 a	1.70	13.4	83.5	5.0	29	0.95	0.81	11.5	4.9	35.8	*	*	3.3	3.8	335	*	9.3	*	7.9	38.3	17.1	38.0
SD 31 b	2.7	18.1	79.3	4.6	97	7.1	4.9	17.7	13.3	73.6	*	13.1	11.7	*	1478	9.6	19.7	*	16.8	45.1	44.2	49.2
SD 39 a	0.26	2.8	78.6	4.8	48	1.34	3.6	9.8	3.9	153	3.8	*	14.4	4.8	60.0	*	21.1	*	8.4	77.8	834	24.7
SD 39 b	2.0	16.8	81.1	4.4	22	8.7	1.53	10.8	5.3	33.0	*	*	9.0	6.7	81.1	7.5	10.3	*	8.5	24.9	25.9	30.0
SD 43 a	0.56	6.2	92.5	4.3	150	1.36	8.6	20.7	8.5	65.0	2.8	*	4.5	*	131	*	22.0	*	6.3	40.0	9.0	*
SD 43 b	1.74	20.6	77.6	3.6	23	10.7	4.0	17.8	8.9	58.3	*	*	6.5	3.5	104	3.9	26.4	*	5.0	35.8	32.0	30.6
SD 50 a	1.01	12.5	84.6	5.3	100	5.7	1.17	23.3	23.4	120	2.5	9.3	29.5	28.2	815	21.9	32.2	*	19.5	120	69.0	78.9
SD 50 b	3.7	35.5	60.8	4.8	152	11.8	6.9	32.5	34.9	147	*	16.1	38.5	42.6	748	25.5	39.4	*	22.0	155	105	96.5
SD 53 a	0.47	4.3	94.7	5.3	50	2.6	2.7	22.4	21.5	103	1.94	9.1	25.1	23.2	475	21.3	23.9	*	14.8	107	52.6	69.5
SD 53 b	2.3	22.7	75.1	5.3	39	11.1	3.3	11.0	11.6	111	*	15.2	30.0	34.2	491	24.5	19.7	*	11.2	133	77.3	82.9

a—before remediation; b—after remediation; EC—electrical conductivity; CEC—cation exchange capacity; OM—organic matter; \*—below detection limit; nd—not determined. Analyst: A.C.T.Santos.

**Appendix E. (a) Geo-accumulation (Igeo) index for metals and a metalloid in upstream sediments, before and after the remediation, from the Senhora das Fontes old uranium mine area.**

(a) Geo-accumulation (Igeo) index for metals and a metalloid in upstream sediments, before and after the remediation, from the Senhora das Fontes old uranium mine area.

Upstream	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Th	U	Zn
SD 16 a	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 16 b	1	4	0	0	0	0	1	0	0	0	5	4	0
SD 19 a	0	1	0	0	0	0	0	0	0	0	3	0	0
SD 19 b	1	4	0	1	0	0	1	1	1	0	5	5	0
SD 21 a	0	3	0	0	0	0	1	0	0	0	4	2	0
SD 21 b	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 24 a	0	2	0	0	0	0	2	0	1	0	3	0	0
SD 24 b	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 25 a	0	2	0	0	0	0	0	0	0	0	3	0	0
SD 25 b	0	2	0	0	0	0	0	0	0	0	3	2	0
SD 28 a	0	1	0	0	0	0	2	0	0	0	3	0	0
SD 28 b	0	2	0	0	0	0	0	0	0	0	4	4	0
SD 29 a	0	2	0	0	0	0	0	0	0	0	2	0	0
SD 29 b	0	2	0	0	0	0	0	0	0	0	3	3	0
SD 30 a	0	2	0	0	0	0	0	0	0	0	3	3	0
SD 30 b	0	2	0	0	0	0	0	0	0	0	2	3	0
SD 34 a	0	2	0	0	0	0	3	0	0	0	4	4	0
SD 34 b	0	3	0	0	0	0	1	0	0	0	4	4	0
SD 35 a	0	3	0	0	0	0	1	0	1	0	4	4	0
SD 35 b	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 36 a	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 36 b	1	0	0	1	0	0	0	0	0	0	5	4	0
SD 37 a	0	3	0	0	0	0	0	0	1	0	5	4	0
SD 37 b	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 38 a	0	3	0	0	0	0	0	0	0	0	5	4	0
SD 38 b	0	2	0	0	0	0	0	0	0	0	4	3	0

a – before the remediation; b – after the remediation.

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

$I_{geo} \leq 0$ practically uncontaminated	0	$3 < I_{geo} \leq 4$ heavily contaminated	4
$0 < I_{geo} \leq 1$ uncontaminated to moderately contaminated	1	$4 < I_{geo} \leq 5$ heavily to extremely contaminated	5
$1 < I_{geo} \leq 2$ moderately contaminated	2	$5 \leq I_{geo}$ extremely contaminated	6
$2 < I_{geo} \leq 3$ moderately to heavily contaminated	3		



(b) Geo-accumulation (Igeo) index for metals and a metalloid in downstream sediments, before and after the remediation, from the Senhora das Fontes old uranium mine area.

Downstream	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Th	U	Zn
SD 1 a	0	4	1	1	1	0	3	1	0	0	5	4	1
SD 1 b	1	4	2	1	1	0	2	1	0	0	5	5	1
SD 2 a	0	3	0	0	1	0	3	0	2	1	3	1	1
SD 2 b	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 4 a	0	3	0	0	0	0	1	0	1	0	4	3	0
SD 4 b	0	4	0	0	0	0	1	0	0	0	4	4	0
SD 5 a	0	3	0	0	0	0	0	0	0	0	4	3	0
SD 5 b	1	4	0	0	0	0	1	0	1	0	5	5	1
SD 7 a	1	4	1	1	1	0	1	1	0	0	5	6	0
SD 7 b	0	4	1	1	1	0	0	1	0	0	5	5	0
SD 8 a	0	4	1	1	1	0	3	1	0	0	5	4	0
SD 8 b	1	4	1	1	1	0	1	1	0	0	5	5	0
SD 10 a	0	4	1	0	0	0	3	0	0	0	4	4	0
SD 10 b	0	4	0	0	0	0	1	0	0	0	5	4	0
SD 13 a	0	3	0	0	0	0	0	0	1	0	4	5	0
SD 13 b	1	3	0	1	0	0	0	0	0	0	5	4	0
SD 31 a	0	2	0	0	0	0	0	0	0	0	3	3	0
SD 31 b	0	3	0	0	0	0	2	0	0	0	3	4	0
SD 39 a	0	4	0	0	0	0	0	0	0	0	4	8	0
SD 39 b	0	2	0	0	0	0	0	0	0	0	2	3	0
SD 43 a	0	3	0	0	0	0	0	0	0	0	3	2	0
SD 43 b	0	3	0	0	0	0	0	0	0	0	3	4	0
SD 50 a	0	4	0	0	0	0	1	0	1	0	4	5	0
SD 50 b	1	4	1	1	1	0	1	0	1	0	5	5	0
SD 53 a	0	3	0	0	0	0	0	0	0	0	4	4	0
SD 53 b	0	4	1	0	1	0	0	0	0	0	5	5	0

a – before the remediation; b – after the remediation.

## References

- Alloway, B.J., 1995. *Heavy Metals in Soils*, 2nd ed. Blackie Academic & Professional, London, p. 368.
- Barros, R.F. de, 1966. O jazigo da Senhora das Fontes. Com. Serv. Geol. Portugal L, 109–129.
- British standard (BS) 7755, 1995. Soil quality. Part 3. Chemical methods section 3.2. Determination of pH. ISO 10390:1995.
- British standard (BS) 7755, 1995. Soil quality. Part 3. Chemical methods section 3.4. Determination of the specific electrical conductivity. ISO 11265:1994.
- Bruno, J., de Pablo, J., Duro, L., Figueiredo, E., 1995. Experimental study and modeling of the U(IV)-Fe(OH)<sub>3</sub> surface precipitation/coprecipitation equilibria. *Geochim. Cosmochim. Acta* 59, 4113–4123.
- Cabral Pinto, M.M.S., Silva, M.M.V.G., Neiva, A.M.R., 2008. Geochemistry of U-bearing minerals from the Vale de Abrutiga uranium mine area, central Portugal. *Neues Jahrb. Mineral.* 185/2, 183–198.
- Cabral Pinto, M.M.S., Silva, M.M.V.G., Neiva, A.M.R., Guimarães, F., Silva, P.B., 2009. Uranium minerals from a Portuguese Variscan peraluminous granite, its alteration, and related uranium-quartz veins. In: Wolfe, Gerhardt H. (Ed.), *Uranium: Compounds, Isotopes and Applications*. Nova Science, New York, pp. 287–318.
- Carlsson, E., Thunberg, J., Öhlander, B., Holmström, H., 2002. Sequential extraction of sulphide-rich tailings remediated by the application of till over, Kristineberg mine, northern Sweden. *Sci. Total Environ.* 299, 207–226.
- Carvalho, P.C.S., Neiva, A.M.R., Silva, M.M.V.G., 2012. Assessment to the potential mobility and toxicity of metals and metalloids in soils contaminated by old Sb-Au and As-Au mines (NW Portugal). *Environ. Earth Sci.* 65, 1215–1230.
- Catalano, J.C., Brown, G.E., 2005. Uranyl adsorption onto montmorillonite: evaluation of binding sites and carbonate complexation. *Geochim. Cosmochim. Acta* 69, 2995–3005.
- Cotelo Neiva, J.M., 2003. Jazigos portugueses de minérios de urânio e sua gênese. In: Ferreira, M.R.P.V. (Ed.), *Engineering Geology and Geological Resources*, 1. Coimbra University Press, Coimbra, pp. 5–76, Book in honour to Prof. J.M. Cotelo Neiva.
- Craft, E.S., Abu-Qare, A.W., Flaherty, M.M., Garofolo, M.C., Rincavage, H.L., Abou-Donia, M.B., 2004. Depleted and natural uranium: chemistry and toxicological effects. *J. Toxicol. Environ. Health Part B* 7, 297–317.
- Decreto Ministeriale, 1999. Approvazione dei metodi ufficiali di analisi chimica del suolo. *SO Gazzetta Ufficiale*.
- Dixit, S., Hering, J.G., 2003. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environ. Sci. Technol.* 37, 4182–4189.
- Dong, W., Brooks, S.C., 2006. Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>) using anion exchange method. *Environ. Sci. Technol.* 40, 4689–4695.
- Duff, M.C., Amrhein, C., 1996. Uranium (VI) adsorption on goethite and soil in carbonate solutions. *Soil Sci. Soc. Am. J.* 60, 1393–1400.
- Duff, M.C., Amrhein, C., Bertsch, P.M., Hunter, D.B., 1997. The chemistry of uranium in evaporation pond sediment in the San Joaquin Valley, California, USA, using X-ray fluorescence and XANES techniques. *Geochim. Cosmochim. Acta* 61, 73–81.
- Duff, M.C., Hunter, D.B., Bertsch, P.M., Amrhein, C., 1999. Factors influencing uranium reduction and solubility in evaporation pond sediments. *Biogeochemistry* 45, 95–114.
- EDM Report, 2008. Concessão para a actividade de reabilitação e monitorização ambiental de áreas mineiras degradadas. Relatório do programa que iam executar, 58–60 pp. [www.edm.pt/images/relcontas1sem2008.pdf](http://www.edm.pt/images/relcontas1sem2008.pdf). For images after the remediation. [www.edm.pt/html/proj-srfontes.htm](http://www.edm.pt/html/proj-srfontes.htm).
- Ferreira, A., Inácio, M.M., Morgado, P., Batista, M.J., Ferreira, L., Pereira, V., Pinto, M.S., 2001. Low-density geochemical mapping in Portugal. *Appl. Geochem.* 16, 1323–1331.
- Ferreira, A.M.P.J., 2000. Dados geoquímicos de base de sedimentos fluviais de amostragem de baixa densidade de Portugal Continental: Estudo de factores de variação regional. In: Unpublished PhD Thesis. Univ. Aveiro, Portugal.
- Food and Agriculture Organization of the United Nations (FAO), 2014. World reference base for soil resources 2014. International soil classification system for naming soils and creating legends for soil map. In: *World Soil Resources Reports*. FAO, Rome, E-ISBN 978-92-5-108370, 181 p.

- Frau, F., Ardaou, C., 2004. Mineralogical controls on arsenic mobility in the Bacchu Locci stream catchment (Sardinia, Italy) affected by past mining. *Mineral. Mag.* 68, 15–30.
- Gál, J., Hursthouse, A.S., Cuthbert, S.J., 2006. Chemical availability of arsenic and antimony in industrial soils. *Environ. Chem. Lett.* 3, 149–153.
- Gómez, P., Garrolón, A., Buil, B., Turrero McJ. 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.
- Gabriel, U., Gaudet, J.P., Spadini, L., Charlet, L., 1998. Reactive transport of uranyl in a goethite column: an experimental and modelling study. *Chem. Geol.* 151, 107–128.
- García-Sánchez, A., Alonso-Rojo, P., Santos-Francés, F., 2010. Distribution on mobility of arsenic in soils of a mining area (Western Spain). *Sci. Total Environ.* 408, 4194–4201.
- Geipel, G., Amaryi, S., Bernhard, G., 2008. Mixed complexes of alkali earth uranyl carbonates: a laser-induced time-resolved fluorescence spectroscopic study: spectrochim. Acta Part A Mol. Biomol. Spectrosc. 71, 53–58.
- Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. *Soil Sci. Soc. Am. J.* 66, 413–421.
- Grosbois, C., Courtin-Nomade, A., Martin, F., Bril, H., 2007. Transportation and evolution of trace elements bearing phases in stream sediments in a mining-influenced basin (Upper Isle River, France). *Appl. Geochem.* 22, 2362–2374.
- Grosbois, C., Meybeck, M., Lestel, L., Lefèvre, I., Moatar, F., 2012. Severe and contrasted polymetallic contamination patterns (1900–2009) in the Loire River sediments (France). *Sci. Total Environ.* 435–436, 290–305.
- Gruan, G., Dia, A., Olivie-Lauquet, G., Serrat, E., 2000. The effects of organic matter and seasonal redox dynamics on chemical weathering: constraints from natural wetland studies. *J. Conf. Abs.* 5, 463.
- Heikkinen, P.M., Räisänen, M.L., 2009. Trace metal and As solid-phase speciation in sulphide mine tailings: indicators of spatial distribution of sulphide oxidation in active tailings impoundments. *Appl. Geochem.* 24, 1224–1237.
- Kabata-Pendias, A., Mukherjee, A.B., 2009. Trace Elements from Soils to Human. Springer, Berlin, p. 450.
- Kaiser, H.F., 1960. The application of electronic computers to factor analysis. *Educ. Psychol. Meas.* 20, 141–151.
- Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* 42, 547–569.
- Larios, R., Fernández-Martínez, R., Álvarez, R., Rucandio, I., 2012. Arsenic pollution and fractionation in sediments and mine waste samples from different mine sites. *Sci. Total Environ.* 431, 426–435.
- Lottermoser, B.G., Ashley, P.M., 2006. Physical dispersion of radioactive mine waste at the rehabilitated Radium Hill uranium mine site, South Australia. *Aust. J. Earth Sci.* 53, 485–499.
- Lottermoser, B.G., Ashley, P.M., Costelloe, M.T., 2005. Contaminant dispersion at the rehabilitated Mary Kathleen uranium mine, Australia. *Environ. Geol.* 48, 748–761.
- Müller, S.N., 1979. Den sediment des Rheins-Veränderungen seit (1971). *Unschau* 79, 778–783.
- Macedo, C.A.R., 1988. Granitóides, complexo xisto-grauváquico e ordovícico na região entre Trancoso e Pinhel: geologia, petrologia, geocronologia. In: Unpublished PhD Thesis. University of Coimbra, pp. 403p.
- Macklin, M.G., 1992. Metal pollution of soils and sediments: a geographical perspective. In: Newson, M.D. (Ed.), *Managing the Human Impact of the Natural Environment*. Belhaven Press, London, pp. 172–195.
- Manning, B.A., Goldberg, S., 1997. Adsorption and stability of arsenic (III) at the clay mineral-water interface. *Environ. Sci. Technol.* 31, 2005–2011.
- Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Eng. Geol.* 60, 193–207.
- Neiva, A.M.R., Carvalho, P.C.S., Antunes, I.M.H.R., Silva, M.M.V.G., Santos, A.C.T., Cabral Pinto, M.M.S., Cunha, P.P., 2014. Contaminated water stream sediments and soils close to the abandoned Pinhal do Souto uranium mine, Central Portugal. *J. Geochem. Expl.* 136, 102–117.
- Neiva, A.M.R., Carvalho, P.C.S., Antunes, I.M.H.R., Santos, A.C.T., Cabral-Pinto, M.M.S., 2015. Spatial and temporal variability of surface water and groundwater before and after the remediation of a Portuguese uranium mine area. *Chem. Erde* 75, 345–356.
- Neiva, A.M.R., Antunes, I.M.H.R., Carvalho, P.C.S., Santos, A.C.T., 2016. Uranium and arsenic contamination in the former Mondogo Sul uranium mine area, central Portugal. *J. Geochem. Explor.* 162, 1–15.
- Nelson, D.W., Sommers, L.E., et al., 1996. Total carbon, organic carbon, and organic matter. In: Page, A.L. (Ed.), *Methods of Soils Analysis, Part 2, 2nd ed.* Agronomy, 9. American Society of Agronomy, Inc., Madison, WI, pp. 961–1010.
- Payne, T.E., Davis, J.A., Waite, T.D., 1996. Uranium adsorption on ferrihydrite-effects of phosphate and humic acid. *Radiochim. Acta* 74, 239–243.
- Pinto, M.M.S.C., Silva, M.M.V.G., 2005. Contemporary Reviews of Mine Water Studies in Europe, Part 3–Portugal. In: C. Wolkersdorfer, R. Bowell (Eds.), *Mine Water and the Environment*. Journal of the International Mine Water Association, Springer.
- Pinto, M.M.S.C., Silva, M.M.V.G., Neiva, A.M.R., 2004. Pollution of water and stream sediments associated with the Vale de Abrutiga uranium mine, Central Portugal. *Mine Water Environ.* 23, 66–75.
- Porcelli, Di Anderson, P.S., Wasserburg, G.J., Ingri, J., Baskaran, M., 1997. The importance of colloids and mines for the transport of uranium isotopes through the Kalix River watershed and Baltic Sea. *Geochim. Cosmochim. Acta* 61, 4095–4113.
- Ribera, D., Labrot, F., Tisnerat, G., Narbonne, J.F., 1996. Uranium in the environment: occurrence, transfer and biological effects. *Rev. Environ. Contam. Toxicol.* 146, 53–80.
- Schöner, A., Noubactep, C., Büchel, G., Sauter, M., 2009. Geochemistry of natural wetlands in former uranium milling sites (eastern Germany) and implications for uranium retention. *Chem. Erde* 69 (S2), 91–107.
- Schaller, J., Weiske, A., Dudel, E.G., 2011. Effects of gamma-sterilization on DOC: uranium and arsenic remobilization from organic and microbial rich stream sediments. *Sci. Total Environ.* 409, 3211–3214.
- Sheppard, S.C., 1992. Summary of phytotoxic levels of soil arsenic. *Water Air Soil Pollut.* 64, 539–550.
- Sparks, D.L., 2003. *Environmental Soil Chemistry*. Academic Press, San Diego, pp. p352.
- Thomas, G.W., 1982. Exchangeable cations. In: Page, A.L. (Ed.), *Methods of Soil Analysis, Part 2, Second Edition*. Agronomy Monograph. American Society of Agronomy, Madison, WI, p. 9.
- User manual, 2001. Jobin Yvon ICP spectrometers, version 3.0. Reference: 31088486, January 2001, pp. 20–23.
- Waggit, P., 2008. Uranium mining legacies remediation and renaissance development: an international overview. In: Merkel, B.J., Hasche-Berger, A. (Eds.), *Uranium Mining and Hydrogeology*. XXII. Springer, 958 p. <http://www.springer.com/978-3-540-87745-5>.
- Zielinski, R.A., Otton, J.K., Wanty, R.B., Pierson, C.T., 1987. The geochemistry of water near a surficial organic-rich uranium deposit northeastern Washington State, USA. *Chem. Geol.* 62, 263–289.